STUDIES OF ANTIOXIDANTS AND INHIBITOR MECHANISMS AT ELEVATED TEMPERATURES

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FOREWORD

This report was prepared by James W. Cole, Jr., Professor of
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Contract AF 18-(603)-103. The writer was director of the project
and takes this opportunity to express his personal appreciation as
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PUBLICATION REVIEW

This report has been reviewed and is approved.

ABSTRACT

The objective of this research is a fundamental study of the behavior of some selected antioxidants and corrosion inhibitors in di-(2-ethylhexyl) sebacate under oxidizing conditions at 204^0C alone and in the presence of metallic copper and copper compounds. Considerable attention was given to kinetic-mechanistic studies with phenothiazine and its derivatives, with phenothiazines containing radioactive sulfur-35 and with N-carbon-14-methyl phenothiazine. Important steps in the behavior of the phenothiazine type are rapid oxidation and oxidative de-methylation of the additives to form oxy-species capable of inhibiting free radical chains, peroxides and thermally activated intermediates in the oxidation of the di-ester. The oxy-species from those phenothiazines having antioxidant activity undergo further oxidation and interactions to form inactive and sparingly soluble products containing sulfur. This may be the material known as "phenothiazine dirtiness". It occurs with all of the derivatives examined.

A second phase involved oxidations with some amines and pyridine derivatives, especially the dipyridylamines. The presence of copper and certain copper compounds enhances the oxidation inhibiting properties of the additives. Metal coordination complexes appear to be a factor in the mechanism either as active antioxidant species, or as starting points and catalysts for the generation of oxy-species which act as the antioxidants. Related to this is the behavior of the two oxidation states in copper, and shifts between the states, which might give rise to magnetic phenomena having some influence in the antioxidant mechanism. The syntheses and behavior of twenty-seven new compounds are described.

TABLE OF CONTENTS

Introductions and Acknowledgements

The interest in studying high temperature antioxidants in synthetic lubricants of the diester type began here in 1950 when a group negotiated a contract with the United States Air Force through the Materials Laboratory, Wright Air Development Center, WCRTR-1 and WCRTR-2. During the period from 1951 until October 1957 an extensive study was made to determine the oxidation patterns of a large number of systems. The point of view was more to evaluate as large a number of promising compounds as possible in a variety of fluids including esters, silicates, silicones, mineral oils and some organic phosphates, with the hope of finding new combinations for end uses. However, considerable attention was given to mechanism studies of the phenothiazine-di-(2-ethylhexyl] sebacate system. In addition a comprehensive survey of the literature on antioxidants and anti-corrosive additives for lubricants at elevated temperatures was prepared to cover work done up to May 1954. In connection with the experimental work there were eight annual reports prepared and made available through ASTIA and the Office of Technical Services, U.S. Department of Commerce. A number of papers were also published in the chemical literature. A list of these reports and papers is included in the bibliography at the end of this report.

As a result of the extensive testing and evaluation program, new interest was aroused in learning more about oxidation and inhibitor mechanisms, and to elucidate the behavior of metal catalysts, especially copper. In July 1956 work was begun under the Contract for which this document is the final report. In the initial stages there was some overlapping with the original contract of WADC and also it seemed desirable to re-check certain phases of the earlier work having to do with mechanism studies. The work to be described herein will be sub-divided for convenience into several sections:

Section I - is concerned with a review of some of the experiences with phenothiazine and its derivatives in di-(2-ethylhexyl) sebacate in the neighborhood of 200^0C. This is done in order to establish a base line for comparison of other systems and to point out the complex nature of the problem. In this section some new experiences will be described with radioactive tracers in the phenothiazine antioxidants. The use of a variety of

approaches has led to the conclusion that the substance originally added is not necessarily the active antioxidant. Evidence will be summarized to show that a substance such as phenothiazine may become active as an antioxidant as a result of its reaction with oxygen itself to form oxy-species which have antioxidant activity. With some other type of amines, such as 2, 2'-dipyridylamine, it appears that the presence of copper serves to activate the substance to form species which serve as oxidation inhibitors. Speculation on the possible mechanisms will be included in this section and a later section having to do with the amines.

Section II is concerned with the experiences with amines and especially compounds related to pyridine, with most attention given to dipyridylamine and its derivatives. This particular type of substance has very little antioxidant activity when present alone in a diester, such as di-(2-ethylhexyl) sebacate in the neighborhood of 200^0C. However, in the presence of copper, both as the metal and compound, there seems to be a significant enhancement of the antioxidant activity as measured by changes in the kinematic viscosity. The effect is also shown in the presence of a low volatile hydrogen acid. Coordination complexes of copper, perhaps in mixed oxidation states, give the most dramatic oxidation retarding effects and apparently play a significant role either as inhibitors or as catalysts for the generation of species possessing antioxidant activities.

In this section where the amines are to be compared, a viscosity index system will be employed for quick comparisons of the oxidation patterns. A value of 100 in the viscosity index indicates that the system is essentially equivalent to the uninhibited fluid. The lower the index number the greater is the effect of the additive in retarding increases in viscosity. The work here indicates that the phenomenon of the activation of an amine system by copper metal is considerably more general than originally suspected. While there is considerable variation among the various amines, the dipyridylamines for the most part showed the most interesting general behavior pattern. However, within the limits of accuracy of the experimental methods the most favorable system for practical purposes cannot yet be selected. A new approach to

comparison of additives will be needed in order to show the next order of differences. There is also much to be desired in the techniques of preparing and handling and describing the effects of the metals. There appeared to be very little difference in the effect of a copper surface as long as the surface had been cleaned with a solvent and treated with a fine grade of metal polishing paper. Some experiences are noted with electro-plating and electro-polishing of copper surfaces but the differences are not sufficiently significant to aid in the interpretation of the results.

Section III contains a list of the various additives used together with probable structural formulas and the sources of the substances. For those synthesized in the Cobb Chemical Laboratory of the University of Virginia, twenty seven of those synthesized appear to be new compounds.

Section IV Literature Cited.

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SECTION I - Antioxidant Mechanism Studies on Antioxidants of the Phenothiazine Type.

(a) Background. The initial purpose was to study antioxidants and oxidation inhibitors for lubricants and hydraulic fluids of synthetic origin at temperatures in the neighborhood of and above 200°C, in the presence and absence of metal catalysts. The literature survey (5) revealed about 2000 pertinent reports on antioxidants at elevated temperatures. However, discussions in the literature of mechanisms of the additive actions in terms of identifable chemical substances were scarce even for systems at lower temperatures. The system phenothiazine-bis-(2-ethylhexyl)-sebacate was selected because of the outstanding antioxidant activity of phenothiazine at lower temperatures and the interest in synthetic lubricants of the di-ester type. In a definitive study of the mode of action of phenothiazine in a diester fluid, at temperatures up to 175°C, Murphy, Ravner and Smith (14) postulated a peroxide-inhibiting mechanism, involving resonance-stabilized free radicals at the heterocyclic nitrogen, formed by rupture of the N-H bond. This view must be modified at higher temperatures in light of the present experiences.

It was noted early in our work at 204°C that phenothiazine rapidly formed oxygenated species (17). The complexity of the oxidation in the neighborhood of 200°C and higher necessitated a multi-prong attack. In oxidations of organic liquids at moderate temperatures a chain mechanism with hydroperoxide consumption has been generally assumed to be a rate determining step (17). Hence, an interpretation of the action of oxidation inhibitors, when there is regeneration of the inhibiting species, requires a mechanism whereby oxygen at a higher energy level can be subsequently released at a lower energy level. This presumably is the case where there is a well defined induction period with only slight oxidation of the medium during this period.

The postulation of Murphy and others (14) for oxidations in the phenothiazine-bis-(2-ethylhexyl) sebacate system up to 175°C is consistent with this, but their mechanism postulating species derived from phenothiazine did not incorporate our findings of an initial rapid, approximately first-order reaction of phenothiazine with oxygen, nor of an oxidative dealkylation with

nitrogen compounds substituted with alkyl groups (11). Moreover, we found both the methyl and ethyl derivatives to have at least equal antioxidant activities to the parent compound. However, they (14) reported varying antioxidant activities at 175°C for phenothiazine-5-oxide and phenothiazone-3, 7-hydroxy-phenothiazone-3 and for some of the nitrogen and ring substituted phenothiazines. Their hypothesis of resonance-stabilized free radicals and ions can be extended to account for the behavior of the oxyge nated phenothiazines. These species appear to possess the active centers for oxidation inhibition (1,10,11). The postulation of active centers in oxygenated species in the phenothiazine type of antioxidant is consistent also with Kroger's hypothesis (18) of active cente.s in inhibitor molecules for oxidation in hydrocarbons up to 175°C. Some rough conductance measurements on mixtures resulting from the oxidation in the system of interest herein indicates species may also be present of the quinone, and semi-quinone, ion-typed as postulated by Gemant (19).

In oxidations of a fluid containing an oxidation inhibitor, understanding of the mechanism of the oxidation of the medium is desirable, but not vital to the understanding of inhibitor action (16). Murphy and Ravner (20) showed the oxidation of diesters in the range 125-145°C to be autocatalytic. The square root of the oxygen absorbed was a direct function of the peroxide concentration which increased to a maximum and then dropped sharply. We also observed this type of peroxide effect at 200°C, but to a less extent. Further, the concentration of peroxides decreases rapidly at higher temperatures. At 200°C the rate of uninhibited oxidation of bis-(2-ethylhexyl) sebacate was more rapid but the indications are that the rates were in qualitative agreement with the square-root function of the oxygen absorbed. As the oxidation temperature increased above 200°C, the length of the inhibited induction period decreases approximately logarithmically. Above 240°C the effect of additives is mainly to decrease somewhat the general rate of oxidation of the di-ester. This rate is very sensitive to the experimental conditions of the oxidation. It is suggested that the over-all oxidation rates, as the temperatures are increased of the inhibited oxidation of a di-ester, are associated with competing mechanisms involving peroxides, free radicals and other thermally promoted energy-rich species. This view is consistent with the postulations of Rigg and Gisser (17).

In the temperature range 190^0-260^0C, the rate of thermal decomposition of the di-ester is measurable, but not of an order to interfere in the oxidation rate measurements (15).

(b) **Experimental Oxidations.** The behavior of phenothiazine, its nitrogen and ring substituted derivatives, and some related types of compounds, in bis-(2-ethylhexyl) sebacate are shown in Table I, where the antioxidant effectiveness of each is compared for a 72-hour oxidation period. In Section I, the measures of the relative antioxidant effectiveness of an additive for a given temperature and oxidation time are: per cent increase in kinematic viscosity of the fluid at 55^0C, the actual increase in acidity and the weight of insoluble matter after filtration on a sintered crucible and washing with iso-octane and acetone (13). In these particular oxidations, the liquid volume was 25.0 ml in a 125 ml test cell fabricated from a 34/45 ℑ outer member ground joint. This was connected to an overhead condenser with a delivery tube for dry air inside extending to the bottom of the cell. When desired the exhaust gases were trapped in suitable solvents. An aluminum thermostated furnance with a fusible alloy in the cell sockets gave temperature control within 2^0C at 204^0C. The quantities of additives were equivalent to 0.25 grams of resublimed phenothiazine per 25 ml (ca. 0.05 molar).

With the effective antioxidants the quantity of insoluble matter is not strongly affected by the location of substituents. The roughly equivalent quantities of insolubles suggest that the final oxidation products are probably of the same type. The role of substituents on nitrogen is also relatively unimportant as most of the N-substituted derivatives had antioxidant activity approximating the parent compound. The relative contributions of the heterocyclic atoms on activation of the aromatic ring systems is indicated in Table I, by the greater antioxidant activity of some of the amines over the analogous thio compounds. Some evidence, however, indicates that sulfur compounds may increase in antioxidant activity with an increase in temperature (11,12,13). The sulfoxides present a somewhat anomalous situation in that phenothiazine-5-oxide appears to be as effective an antioxidant

as the parent compound. However, in a sulfoxide, also containing a nitrogen substituted methyl or ethyl group, the antioxidant activity was diminished.

A more quantitative measure of the relative antioxidant effectiveness is the length of the oxidation induction period (9,10,11) when this is reasonably well defined. In the initial stage of an oxidation with phenothiazine at 204°C, there was a rapid but relatively small increase in the acid content and kinematic viscosity, which was roughly proportional to the concentration of phenothiazine. During this period the color changed from pale yellow to red. This was followed by a period of little change in properties except a deepening of the red color, and the formation of a dark brown to black, finely divided solid. This is sometimes called "phenothiazine dirtiness". The length of this induction period is proportional to the concentration of phenothiazine and is a logarithmic function of the temperature. At the end of the induction period, the acidity and viscosity increased rapidly and the general characteristics were those of uninhibited oxidation of the medium. In the temperature range 190°C to about 240°C the initial period of change is interpreted as reaction between phenothiazine and oxygen to form oxygenated species, plus only a slight oxidation of the medium. During the remainder of the induction period there is a much slower reaction of the oxygenated species to form inactive red-brown polymeric substances and finally dark brown to black insoluble matter. Above about 240°C the effect of the concentration of phenothiazine is mainly to prolong a slower rate of oxidation with a less well-defined induction period, before the faster autoxidation period begins. The derivatives of phenothiazine showed the same general behavior. However, when nitrogen was bonded to a methyl or ethyl group, the relative antioxidant effectiveness was maintained for a longer period as the temperature was increased.

The rate of initial oxidation of phenothiazine was followed in another independent way (1, 9). The decrease in absorbance of phenothiazine at the characteristic maximum (252 mu) with time of oxidation is approximately first order, but there is a slight shift toward longer wave lengths. These changes and the appearance of new maxima at longer wave lengths, have

assisted in relating known oxygenated species to those postulated as active in the antioxidant mechanisms. Some of these active species were identified in the air and photochemical oxidation of phenothiazine in other solvents in another phase of our work (1). From plots of the reaction rate constants derived from plots of the logarithms of the absorbance ratio against time vs temperature, we have calculated the activation energies for the initial process to be approximately 15 kcal. and 10 kcal. in the absence and presence of copper, respectively (9). The relatively low values give some indication of the importance of thermal activation.

The effects of metallic copper was unexpected. The reaction rate' constant for the initial disappearance of the characteristic spectrum of phenothiazine was smaller in the presence of copper at $200^{0}C$, but the activation energy was also lower. This suggests that the metal surface deactivates some of the thermally activated species to decrease the rate of formation of active oxygenated species but that as copper dissolved, the rate is then increased by homogeneous catalysis. The spread in the experimental values in the presence of copper, at higher temperatures suggests that secondary processes are occuring. With dissolved copper compounds the same conclusion is indicated.

The rate of reaction between phenothiazine and pure oxygen was also measured, in a closed, constant-pressure, all glass, apparatus designed to circulate dry oxygen at a fixed rate, through the fluid in an oxidation cell and at the same time measure the rate of oxygen absorbed and the quantities of oxidation products formed. With this circulating system, blends were oxidized containing 0.5%, 1.0% and 3.0% sublimed and recrystallized (from ethanol) phenothiazine, in the middle out of a fluid obtained by a vacuum distillation of platicizer-grade bis-(2-ethylhexyl) sebacate (Plexol 201), Rohm and Haas, Inc.). Some representative date for the rates of absorption of oxygen are plotted on Figure 1. Also shown is the volume of the oxygen required to oxidize any carbon monoxide formed to carbon dioxide in a secondary reaction with copper oxide at $400^{0}C$ incorporated in the closed circulating system. The oxygen needed was calculated from the weight gains of U-tubes in the system containing suitable absorbants for carbon dioxide.

Small amounts of carbon monoxide were detected almost from the beginning of an oxidation run by the color change in a very sensitive palladous silico-molybdate indicating granules in the circulating system. This substance is specific for traces of carbon monoxide (20), when large quantities of volatile hydrocarbons and hydrogen are absent. The absence of equivalent water in the secondary reaction suggests that no significant hydrogen or light hydrocarbons get to the copper oxide. A section of indicating Drierite and silica gel, in the tube section immediately following the oxidation cell, collected water formed in the initial reaction of phenothiazine and absorbed traces of ambient substances.

The data indicate that a direct proportionality exists between the initial quantity of oxygen absorbed and the concentration of phenothiazine. After the correction for the oxygen used to form carbon dioxide it is apparent that about one mole of oxygen is used per mole of phenothiazine during the initial rapid oxidation. A rough approximation of the amount of water formed in the initial oxidation of phenothiazine based on the length of color produced on the Drierite compared with color changes produced by known quantities of water when the water vapor was brought into contact with the cobalt chloride indicator under analogous conditions, also corresponds to about 1 mole of phenothiazine per mole of oxygen.

A conventional kinetic analysis of the oxygen absorption rate data at 204^0C supports the postulation that the initial oxidation process is due primarily to changes in phenothiazine. The specific reaction rate constant of $k = 0.18 \ hr^{-1}$, assuming a first order reaction with respect to phenothiazine, agrees with the constant derived from ultra-violet rate change in absorption spectra of the same system under oxidation (9, 10, 11). The sharp break in the idealized oxidation curve (dotted in Figure 1), supports the view that at least two processes are occuring. A kinetic analysis of data for the slow period of oxidation (induction period) shows that the process occuring is probably not associated with the concentration of phenothiazine as long as some of the active species are present. A value for the reaction rate constant at 204^0C, for this period of inhibited oxidation, assuming it to be

due primarily to changes in the diester, in an excess of oxygen, is $k = 0.005$ hr^{-1}. This is at least a tenfold faster process than the secondary oxidation of phenothiazine occuring as the oxy-species are expended and must be associated with a slow oxidation of the fluid medium. A chromatographic separation of the mixture during the slow period, followed by comparison of the ultra-violet spectra of the fractions with known substances confirmed the presence of substances related to oxidized phenothiazine such as phenothiazine-3 (1). Moreover, this substance itself showed at least equivalent antioxidant activity to the parent compound, note Table I. There is also some indication of small amounts of an ester of phenothiazine with fragments from the medium. This type is probably more volatile than the other derivatives of phenothiazine. The products arising from further oxidation of the oxy-phenothiazines, such as 3-hydroxy-phenothiazone-3 (thionol) had very little, if any, antioxidant activity.

(c) <u>Peroxide Effects in the Systems under Oxidation.</u> In the absence of phenothiazine, bis-(2-ethylhexyl) sebacate reacted rapidly with oxygen but the rate became less rapid with time. This suggests that substances are formed which tend to retard the oxidation of the diesters . by inhibiting formation of peroxides. The pattern of oxidation of the fluid containing phenothiazine after the end of the induction period has much similarity to that of the uninhibited fluid. At the end of the induction period there is a very rapid rate of oxygen absorption which slows down after about the same quantity of oxygen has been taken-up as in the uninhibited fluid.

A comparison at 204°C of the oxidation patterns with the peroxide analyses of the oxidized mixture revealed interesting phenomena. In bis-(2-ethylhexyl) sebacate alone, there was a large increase in peroxide content immediately upon starting dry air into the hot fluid, followed by an approximate exponential decrease in the peroxide content of the uninhibited fluid, Figure 2. The acidity in the diester medium increased with time but not strictly at a rate equivalent to the peroxide behavior observed. In the presence of copper, the otherwise uninhibited liquid, did not exhibit as great an initial increase in peroxides, but showed a lower and more sporadic peroxide content up to about 60 hours where a large increase occurred.

The peroxide effects are apparently not thermally promoted, as such, because no measurable peroxides were detected when nitrogen was used and an increase in temperature decreased the apparent concentration of peroxides.

The effect of phenothiazine on the accumulation of peroxides at 204^0C, was also interesting, Figure 2. With 0.1% phenothiazine no measurable peroxides were detected during a 72 hour run. As the concentration was increased the qualitative effect was to increase the apparent peroxide content with some induction period being evident. The peroxide numbers of some known substances are: phenothiazine, 0.0, N-methylphenothiazine, 1.5, phenothiazine sulfoxide 3.5, phenothiazone-3, 0.0, N-methylphenothiazine sulfoxide 1.5, the dark red intermediate oxidation products of phenothiazine, 24. The small values for the pure compounds may be due to slight photochemical oxidation (1). The large value for the intermediate oxidation product supports the existence of oxygenated species as possible contributors to the antioxidant mechanism.

The composition of the inactive oxidation products of phenothiazine are complex. Micro analyses of the dark brown to black insoluble matter formed during the induction period showed approximately two atoms of oxygen per phenothiazine moiety. Analyses of the insoluble matter obtained after the induction period cannot be ascribed even to approximate compositions because of the contribution from oxidation products of the diester. A molecular weight determination of some red-brown matter obtained by a chromatographic separation of the oxidized mixtures, indicate that a unit containing about four oxygenated monomers is still fairly soluble in the diester. Attempts to inhibit the formation of the "phenothiazine dirtiness" so far have not been fruitful. Hence, it appears that phenothiazine expends its antioxidant activity through formation of oxygenated polymeric substances which precipitate at about 5 units.

(d) Oxidations with S^{35} and C^{14} Labelled Phenothiazines. Oxidations with these radioactive compounds, S^{35}-phenothiazine, N-methyl, S^{35}-phenothiazine and N-C^{14}-methyl phenothiazine, in bis-(2-ethylhexyl) sebacate, were conducted, both in the circulating oxidation apparatus, and in a test cell with dry air or oxygen flowing through the thermostated fluid under a reflux

condenser leading to traps. In a series of runs to measure the rate of formation of insoluble matter at 204°C, air oxidations were performed in 25 ml of bis-(2-ethylhexyl) sebacate containing 0.25 grams S^{35}-phenothiazine (0.05 molar) for varying times. After oxidation, each sample was filtered on a sintered-bottom crucible and the residue washed first with iso-octane and then with acetone. After drying at about 100°C the weight of the solid was expressed as percent acetone-insoluble. The quantity of sulfur in the solid was calculated from the counts per minute, calculated back to zero time of the standards. Check chemical analyses on representative portions by a Parr Bomb oxidation and weighing of $BaSO_4$ showed that the radiochemical analysis for sulfur in the solids was within 10% of the chemical analysis. Where indicated, micro-analyses for carbon, hydrogen and nitrogen were performed on the samples for additional checks.

With S^{35}-phenothiazine and N-methyl-S^{35}-phenothiazine, only a very slight radioactivity was detected in the exhaust. This was associated with a red liquid entrained in the ambient air. A trace of activity in a sodium hydroxide trap appears to arise from elementary sulfur in the phenothiazine as an impurity. Monitoring of the rates of disappearance of radioactivity in the fluid and the subsequent appearance in the acetone insoluble portion lead to reaction rate constants showing the rate at which the active antioxidants species were lost from the system. For S^{35}-phenothiazine, $k = 0.0006$ hr^{-1} (184°C), 0.0008 hr^{-1} (204°C) and 0.002 hr^{-1} (224°C). These values correspond to an activation energy of approximately 12 kcal per mole. A corresponding reaction rate constant of 0.0003 hr^{-1} was obtained only at 204°C for N-methyl S^{35}-phenothiazine.

Radiochemical monitoring of the oxidation of C^{14}-methyl phenothiazine showed a first order loss of the methyl group into the exhaust with $k = 0.017$ hr^{-1} (184°C), 0.05 hr^{-1} (204°C) and 0.17 hr^{-1} (224°C). This process corresponds to an activation energy of approximately 25 kcal per mole. In the presence of copper the activation energy dropped to about 16 kcal per mole.

An interesting aspect of the sulfur count is that at approximately the time, corresponding to the end of the oxidation induction period measured

independently, there was a sharp decrease in the quantity of radio active sulfur containing substances in the liquid phase. This suggests that the amount present just before the end of the induction period might be the approximate equilibrium concentration, 0.06% of active species needed at 204°C for maintaining the oxidation induction period.

The oxidation behavior of N-C^{14}-methylphenothiazine in bis-(2-ethylhexyl) sebacate, involving an approximate first-order loss of activity from the liquid and no significant accumulation of C^{14} in the solids, coupled with appearance of the activity in the exhaust, a slower rate of oxygen consumption, and formation of colored oxy-species, indicate that the rate determining steps are related to oxidative demethylation followed by further oxidation of the same nature as with phenothiazine itself, to form oxygenated species as the active antioxidants. In the presence of nitrogen gas only a very slight demethylation was detected which might be attributed to thermal effects. Under this condition, the major loss of C^{14} count in the heated fluid was from entrainment of unreacted N-methyl phenothiazine in the flowing nitrogen. In the presence of oxygen, the traps and absorbers showed C^{14} activity as, carbon monoxide, aldehydes and/ or ketones and low boiling hydrocarbons.

(e) Conclusions-Section I. The mode of action of the phenothiazine-type as an oxidation inhibitor in a thermally stable diester cannot be ascribed to the behavior of any single species in the temperature range 175°-260°C. The evidence favors oxygenated phenothiazines acting as peroxide chain inhibitors. free radicals absorbers, and centers for deactivation of thermally activated molecules and radicals. The presence of a variety of colored products in an oxidation mixture, ranging from violet, through blue, to green, red and brown leads to the conclusions that temperature and catalysts, especially metals, play important roles in determining the equilibrium concentration of a particular active species. The thermal deactivation process becomes more important as the temperature increases from 190°C. Above 240°C this factor is much more prominent and gives the effect of a negative catalyst or oxidation retarder rather than a promoter of an induction period.

The most interesting effects observed were at 204^0C where the rate of initial oxidation of phenothiazine (k= 0.15 hr^{-1} to 0.18 hr^{-1}) was separated, and the oxygen equivalents determined. Likewise measurable were the rates of oxygen absorbed as a slow process during the induction period, k = 0.005 hr^{-1}. This represents a faster process than the actual expending of the active species with k = 0.0008 hr^{-1}. The activation energy of about 15 kcal for the initial reaction of phenothiazine with oxygen and the slightly lower value of 12 kcal, for the expending of the oxygenated species are interpreted to indicate that phenothiazine will not gain in effectiveness as the temperature is increased. With 10-methylphenothiazine there is some gain in relative antioxidant effectiveness as the temperature is raised. This is in line with the larger value of 25 kcal for the initial oxidative demethylation as the rate determining step process. Hence, the contribution of simple free radicals of the type formed by removal of a hydrogen atom, or a radical, from the heterocyclic nitrogen of phenothiazine to the antioxidant action appears less important at the elevated temperatures of this study than at 175^0C (14).

Any proposal of a specific mechanism to account for all of the complex behavior in the phenothiazine-bis-(2-ethylhexyl] sebacate system under oxidizing conditions at elevated temperatures involves conjecture. The evidence suggests that definite oxy-species contribute to the oxidation inhibition but additional study is needed to identify them in equilibrium concentrations and their temperature dependents. It has been postulated that free radicals and free radical ions along with semi-quinones and their ions can act as chain stoppers and peroxide inhibitors (14). The data here also suggest that species with centers of high electron density, as found in quinones and phenothiazone-3, may act as centers for chain breaking and "oxygen-re-juvenators". The half-lives of the various species would be very difficult to measure, hence it cannot be postulated as to which might make the more significant contribution on the basis of existing experimental data.

It might be speculated that the major proportion of active species are related to phenothiazone-3, its semi-quinone and possibly ions of these. The antioxidant activity of phenothiazine-5-oxide and its presence during a

stage of the oxidation suggests that this is an intermediate in the route to phenothiazone-3, and to the semi-quinone and ions (1). However, the apparent low antioxidant activity of the nitrogen substituted phenothiazine-5-oxide presents an anomaly. A substituent on the nitrogen apparently stabilizes the sulfoxide so that it does not form active species before it undergoes further oxidation. Phenothiazine-5-dioxide showed no significant antioxidant activity at 204°C and appears to accelerate oxidation at 175°C (14). The role of 2-hydroxy-phenothiazone-3 (thionol) in the antioxidant scheme does not seem important at elevated temperatures. It did not have equivalent antioxidant activity to the parent compound either at 204°C as in previous tests, nor was it postively identified in any of our oxidized mixtures (1). Moreover, it probably would not be stable at the elevated temperatures of the present work and if formed during the oxidation it might rapidly react further to form esters, ethers and polymers. Some support of this speculation comes from the nature of the soluble polymeric substances isolated with about 4-5 oxygenated phenothiazine units. Microanalyses of the solids formed on longer oxidations also showed increasing carbon and oxygen and lower nitrogen.

Radiochemical analyses of the solids showed a gradual decrease in the percentage of sulfur present. A saponification of the insoluble portion obtained after the conclusion of the induction period, gave indication of a linkage with a moiety from the diester. The changing nature of the solid makes it impossible at present to assign a definite composition to the so-called 'phenothiazine dirtiness''. However, the formation of the equivalent quantities of the acetone insoluble fractions indicates that the final oxidation products may be of the same type for derivatives of phenothiazine. From the practical viewpoint, this would indicate that further study of phenothiazine derivatives in diesters may not be worthwhile when the purpose is to acquire an antioxidant which does not give significant insoluble matter (16). The same might be said for derivatives of lower volatility, such as 7-benzo(c)-phenothiazine at higher temperatures.

The contribution of substituents on the antioxidant effectiveness of the phenothiazine type and on the formation of insoluble matter, is interesting.

With substituents on the heterocyclic nitrogen atom only, the oxidation inhibiting action is generally retained. Methyl- and ethyl- phenothiazines have a slightly greater activity than the parent compound at 204^0C and their effectiveness is more apparent at temperatures higher than 204^0C. With substituents in the ring, it appears that activity is decreased when the 2-position is occupied, especially when electron attracting or repelling groups or steric factors are evident. With electron attracting substitutents in the 3 and 7 positions, the antioxidant activity is retained, provided the sulfur has not acquired an oxygen atom. In 2, 3, 7, 8-tetrachlorophenothiazine, the active positions appear to be blocked, either through the positions being occupied, or rendered inactive by inductive and steric effects. When another benzene ring is fused to phenothiazine as in 7-benzo(c)-phenothiazine, much of the activity is retained apparently through resonance-stabilization of the active centers. With the fused ring in other positions the activity is decreased. It should be emphasized also that clearly defined assignments of the effects of substituents on the antioxidant activity is complicated by the tendency of some substituted phenothiazines to undergo intramolecular rearrangement (23).

It is interesting to note the inductive effects of sulfur and nitrogen on the aromatic ring system. Included in Table I are the results for 2-aminobenzenethiol and some related amines and thio compounds. The substances with both nitrogen and sulfur in the same relative positions approach phenothiazine in antioxidant activity. The compounds containing only nitrogen are much less effective at 204^0C but they do have a greater effectiveness than those containing only sulfur. Phenoselenazine appears less active than phenothiazine at 204^0C, but at higher temperatures its relative activity is greater. These, however, have enhanced attack on copper metal surfaces.

Another clue to the versatility of the phenothiazine-type may be in the apparent changing of its antioxidant activity with temperature and the existence of intermediate species of varying activity formed by oxidation and the removal of a N-substituent at different rates. In the medicinal uses, the existence of complex catalysts and active species of varying complexities are well known and it is not unreasonable to speculate that the phenothiazines offer many

attractive centers of activity under the various conditions of metabolism. There is a need for thermodynamical data on the various species which have been identified before accurate predictions can be made of the relative stability of each and on the possibilities of activation and deactivation with changing temperatures and catalysts. This approach should be a future step in the studies on antioxidant and oxidation inhibitor mechanisms.

The outlining of model reactions to explain the antioxidant and oxidation retarding effects of the phenothiazine structure in a diester fluid is not important at this time. While it is possible to propose some model reactions in an attempt to account for the behavior of phenothiazine itself, its nitrogen substituted derivatives and the oxy-derivatives, the evidence indicates too many intermediates to place each in its proper sequence. However, the similarity in the thermal and photochemical oxidations of phenothiazine does lend support to the speculation of electron ejection as the initial step to form active ionic species. This might indicate that the variations in relative antioxidant effectiveness among the derivatives of phenothiazine has a probability of being related to the individual ionization potentials, which are not now known and would be difficult to measure under realistic conditions.

The elimination of the hydrogen, or an R group, from the heterocyclic nitrogen is apparently a rate determining step because with C^{14}-methyl phenothiazine the radioactivity initially goes into volatile products at a measurable rate. This might produce both neutral and charged free radicals which react rapidly with oxygen to form the oxy and peroxy intermediates en route to hydroxy phenothiazine and to phenothiazones. The face that phenothiazone-3 is about as active an antioxidant as the parent substance suggests that further free radicals species are produced from the oxy-compounds and that these species, especially in the presence of an acid, have the ability to retard the rate of oxidation of the medium through stopping free radical chains arising from thermal or photochemical activation of the medium. The oxy-species arising from the initial oxidation undergo further oxidation to inactive 7-hydroxy-phenothiazine (thionol) and finally form

condensation products through reaction of the functional oxygen containing groups on remotely located positions of the phenothiazine moiety. The formation of sludge (phenothiazine dirtiness) arises when the inactive products containing the original ring system reached a stage of condensation or polymerization where they precipitate from the medium. Practically all of the phenothiazine derivatives, which possess antioxidant activity, as well as the active amines, formed sludges as products. The sludge from oxidation of phenothiazine retained the original sulfur atom as shown by the radioactivity of S^{35} in the sludge, even in the presence of copper. Further support of this comes from our unsuccessful attempts to promote an exchange of S^{35} in the heterocyclic ring. All of this indicates a very stable heterocyclic system at least up to $200^{0}C$, even in the presence of metals such as copper.

There is still much which might be learned about the mechanism of behavior of phenothiazine as a high temperature antioxidant through further studies of the effect of variations in the temperatures of oxidation in conjunction with obtaining the infra-red spectra of oxidized samples and perhaps employing some new approaches such as nuclear magnetic resonance. However, in attempts to correlate the behavior of antioxidants it should be remembered that the active antioxidant is not necessarily the parent compound and that a fruitful approach for the future lies in getting more information on the intermediate oxidation product of promising antioxidants rather than simply testing a large number of derivatives having slight variations in structure with the hope that one may possess all of the ideal properties for use in a specific situation. This conclusion is also supported by the behavior of representative groups of amines and ring nitrogen compounds to be described in the next section.

FIGURE I-1.

OXIDATIONS IN THE PHENOTHIAZINE-Di-(2-ETHYLHEXYL) SEBACATE SYSTEM AT 204°C

A. Fluid (0.054 mole) No additive.
B. 0.00062 mole Phenothiazine
C. 0.00125 mole Phenothiazine
D. 0.00375 mole Phenothiazine
E. Secondary Oxidation to CO_2
F. Idealized (Less O_2 for CO_2).
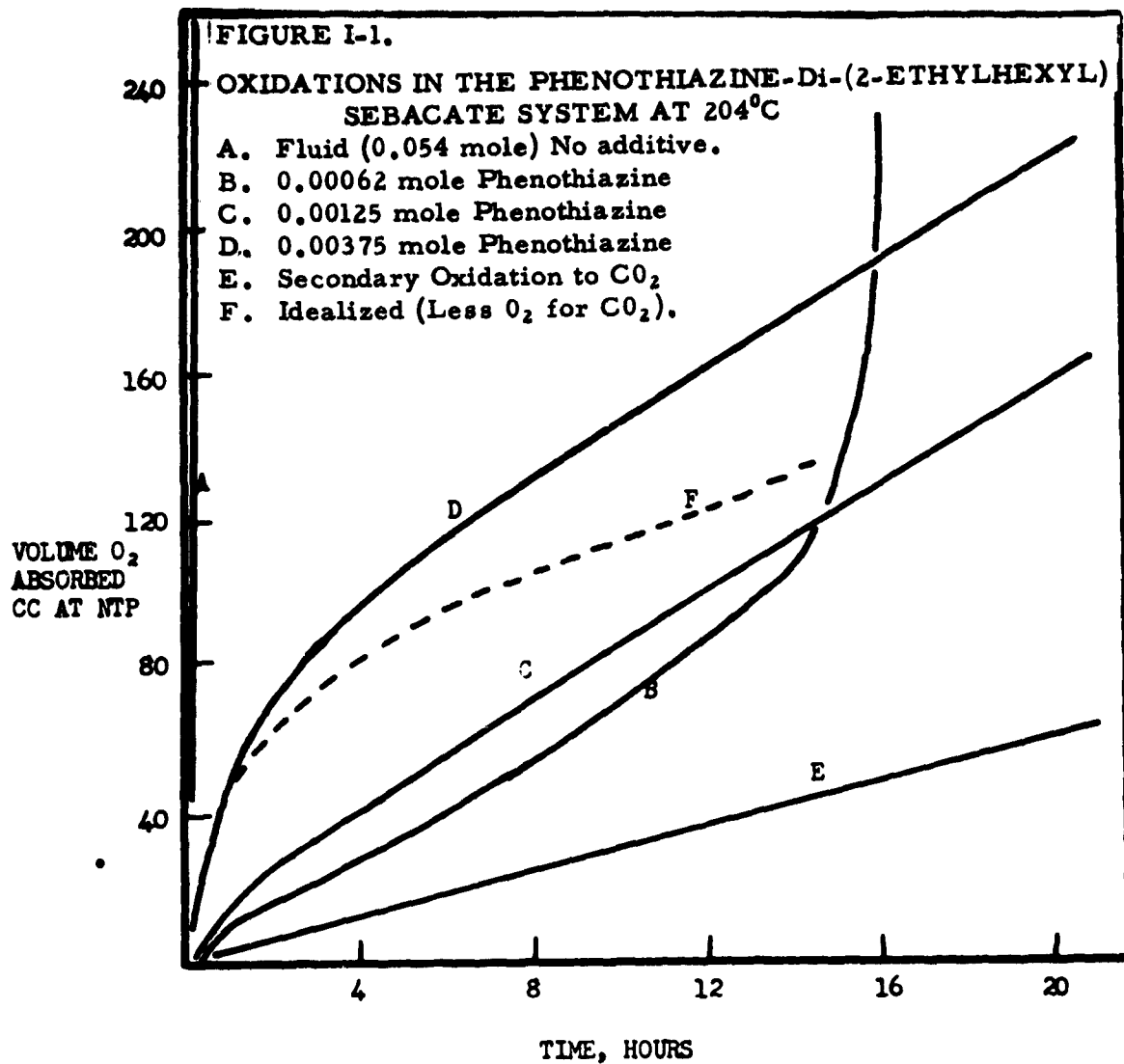
FIGURE I-2.

PEROXIDES IN THE PHENOTHIAZINE DI-(2-ETHYLHEXYL) SEBACATE SYSTEM
At 204°C

A. Fluid (Alone, O)(With Cu ●)
B. 0.1% Phenothiazine on Axis
C. 1.0% Phenothiazine.
D. 6.0% Phenothiazine.
E. 1.0% Phenothiazine with Cu.
F. Nitrogen and Air Interchanged.

FIGURE I-3.
RADIOCHEMICAL ANALYSES OF LIQUID PHASE AFTER OXIDATION
AT 204°C OF DI-(2-ETHYLHEXYL) SEBACATE CONTAINING
PHENOTHIAZINE TYPES.

A. S^{35} Phenothiazine.
B. S^{35} Phenothiazine plus Copper.
C. C^{14} N-Methyl Phenothiazine.
D. S^{35} N-Methyl Phenothiazine.
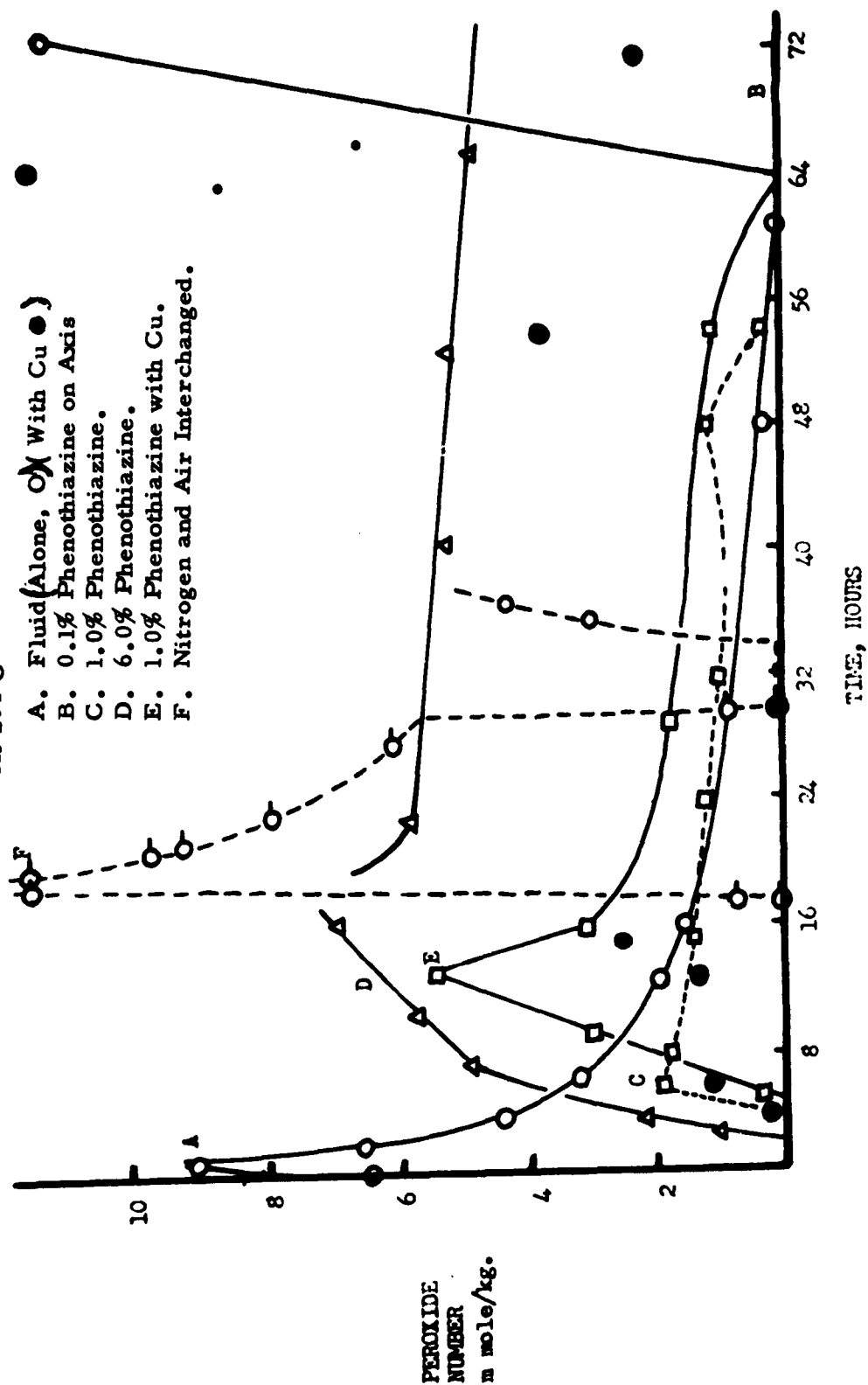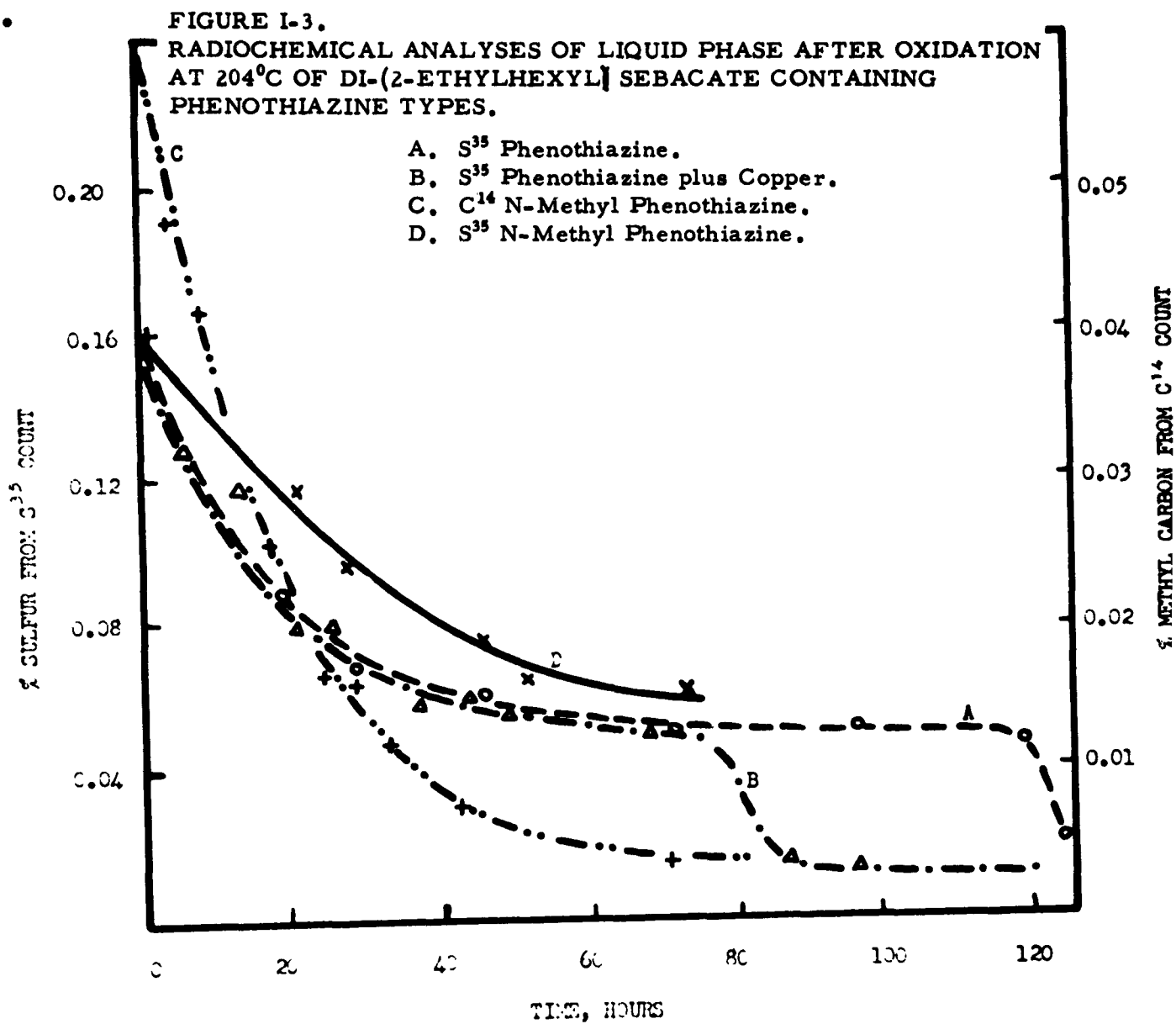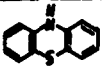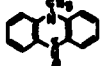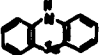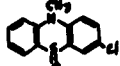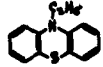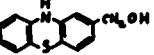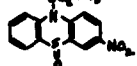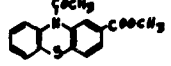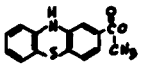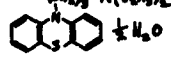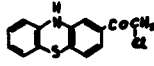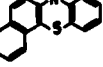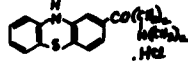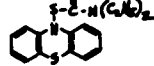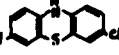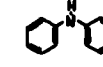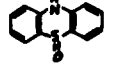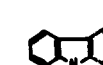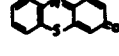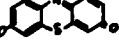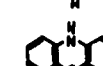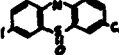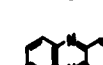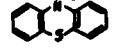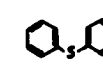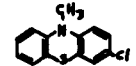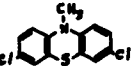
Table I-1. Antioxidant Activity of Phenothiazines and Related Types in Di-(2-ethylhexyl) Sebacate at 204°C.

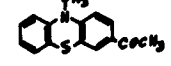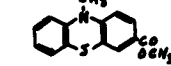| Compound[1]	Kinematic Viscosity Change, %	Neutralisation No.	Acetone Insolubles, gram	Compound	Kinematic Viscosity Change, %	Neutralisation No.	Acetone Insolubles, gram
[structure]	7.6 a/ 7.5 10.4 7.0	4.0 4.0 9.3 4.0	0.23 0.17 0.28 0.27	[structure]	100	30	Excessive
[structure]	9.7	7.0	0.14	[structure]	40	27	0.19
[structure]	53 76	23 24	0.49 0.47	[structure]	4.2	2.3	0.10
[structure]	32	19	0.37	[structure]	51 33	28 21	0.58 0.28
[structure]	53 52 54	26 24 25	0.50 0.39 0.51	[structure]	37	26	0.36
[structure]	8.4 9.1	4.7 5.0	0.16 0.14	[structure]	4.6	2.4	0.16
[structure]	68	35	0.39	[structure]	23	19	0.32
[structure]	103	36	0.30	[structure]	6.3	4.0	0.22
[structure]	6.1	3.0	0.15	[structure]	20	15	0.26
[structure]		Gel		[structure]	67	26	0.01
[structure]	5.6	3.0	0.19	[structure]	70	20	0.03
[structure]	3.2	4.2	0.12	[structure]	35	20	0.03
[structure]	46	23	0.29	[structure]	40	13	0.02
[structure]	56	24	1.2	[structure]	15	10	0.03
[structure]	7.1	4.5	0.13	[structure]	95	26	0.05
[structure]	9.3 5.0 4.6	7.7 2.7 4.0	0.25 0.11 0.17	[structure]	75	20	0.05
[structure]	4.1	5.5	0.26				
[structure]	44	20	0.25	[structure]	80	30	0.05
[structure]	21 10	16 9.1	0.31 0.26	[structure]	95	30	0.04

1/ The quantity of each additive is equivalent to 0.25 gram phenothiazine in 25 ml of fluid. (Analysis after 72 Hours).
a/ In the uninhibited fluid the kinematic viscosity increased about 100% and the neutralization number increased to about 30 %.

SECTION II - Amines as Antioxidants

For a number of years it has been known that certain amines will retard the thermal oxidation of fluids of low volatility. Some amines have also been of interest as corrosion inhibitors (5). In the present work selected amines have been examined with the view of elucidating the effects of structural features and the behavior of metal surfaces. It was observed early in our work that copper in the system undergoing oxidation caused some non-sulfur containing amines apparently to retard the increase in kinematic viscosity of the fluid medium more than the amine in the absence of copper. That is, the presence of the metal apparently caused the amine to have more activity as an antioxidant. The tabulation and discussion of the results with such systems in bis-(2-ethylhexyl) sebacate at 204°C is the objective of this section. The sources and methods of synthesis of the new compounds used will be included in Section III.

(a) Experimental. The experimental method for ascertaining the relative antioxidant activity of additive systems is now a conventional procedure. It was summarized in Section I and described in detail in one of our reports under another contract (6). Briefly, the system under oxidation in a Pyrex Brand cell with appropriate ground fittings and overhead reflux condenser, is heated in an large aluminum block, thermostated furnace with 10 cell sockets, each containing a fusible alloy. The oxygen supply comes through a small diameter tube inside of the condenser and extending below the surface of the heated liquid. When metal surfaces were desired in the oxidizing mixture, washers were supported on the air tube at uniform distances from the bottom of the test cell. The treatment of the washers before and after oxidation is mainly cleaning with solvents and mechanically polishing. The extent of oxidation was measured by determining the percentage change at 55°C in the kinematic viscosity of the fluid system after oxidation and separation of sludges by centrifugation. In a number of cases the formation of acid in the system was measured by titration with potassium hydroxide to a pH of about 8.0. For purposes of comparison the acidity change is described in terms of neutralization number, or milligrams of KOH per liter.

In the following tables the significant results are summarized. In this section, in order to reduce a large amount of data to the same basis, an index number system will be used for comparing viscosity change. In most cases a reference system was included in each of the runs of 10 samples. The index number is 100 times the ratio of the viscosity change of the system under examination to the viscosity change of the blank, or reference system, for the same oxidation times. An index number of 100 corresponds to no antioxidant effect. The smaller the number the greater is the apparent antioxidant activity. Most of the data were for oxidations over the periods ranging from 3 to 60 hours. The additives were compared at molar equivalent concentrations and were in the range corresponding to 0.01% to 0.25% of phenothiazine. Unless otherwise noted the reference system was uninhibited bis-[2-ethylhexyl] sebacate.

The precision and significance of the experimental quantities employed to show the effect of an additive in changing the oxidation pattern of the di-ester are somewhat difficult to describe. For convenience the average values of several determinations will be used in calculating the index number for the changes in kinematic viscosity for the oxidized system. The control was usually a mixture of 0.17 gram of 2, 2'-dipyridylamine in 100 ml of di-(2-ethyl-hexyl)-sebacate or this same additive with test samples of copper metal also present. To show the precision and significance of the index numbers the results of a total of 29 samples were averaged for 0.17 gram of 2, 2'-dipyridylamine in 100 ml of fluid and the same number for this system with three copper washers suspended on the air tube. The next table summarizes these results.

Table II-1. Reference Behavior of 2, 2'-Dipyridylamine at 204°C

Time, (Hours)	3	6	12	24
0.17 gram, no metals	105+ 18	103 + 10	110 + 7	102 + 8
0.17 gram with 3 copper washers	85 + 21	63 + 13	31 + 6	21 + 5

Reference to this table should be made when comparing the various systems to be tabulated later. The reference value indicate that the precision increases with longer periods of oxidation. The shorter sampling times, however, are useful to show the general course of the oxidation, especially in the early stages, and to help in pointing up the most effective additive systems.

In general the viscosity index will be used as the basis for comparison, because there was some increase in acidity with each of the amines which is not yet explainable. Briefly, it appears that acidity has some relationship to both the acceleration and to the inhibition of oxidation, but the situation is complex as will be noted in the following tables where a mineral acid was actually added to the mixtures under oxidation.

In the tables to follow, much of the information was obtained on samples drawn from the hot mixture at 3, 6, 12 and 24 hour intervals. The index numbers for 60 hours represent the undisturbed mixture under oxidation at 204°C for 60 hours. At the end of this time the mixture was allowed to cool and the analyses performed. The CCL No. (Cobb Chemical Laboratory) is the code number of the compound used as the additive. The figures under concentration are grams of additive per 100 ml of diester fluid. Each horizontal line represents a run at 204°C for the mixture. When two are more additives are listed for a single line, the run is for a mixture of additives at the concentrations indicated. The presence or absence of the test metal washers is indicated under the heading "Metals". The number before the symbol indicates the number of washers used.

(b) Discussion. As will be noted in Table II-2 there are some interesting, but also perplexing experimental results. The main purpose of the tabulations are (1) to show the effects of additional substances along with an additive under examination as a possible antioxidant, and (2) to note the behavior of derivatives and related substances of certain of the amines which had exhibited interesting oxidation patterns in di-(2-ethylhexyl) sebacate at 204°C.

In comparing the behaviors of the various systems, it should be noted that the experimental procedure has limitations because of the number of variables involved. This is especially striking for the short oxidation periods

(3 and 6 hours) because changes seem to occur rapidly when the fluid system is brought quickly from the initial mixture prepared at room temperature to the temperature of $204^{\circ}C$ of the thermostated furnaces. However, there are sufficient differences in most of the values of the viscosity indexes to show the behavior of the system relative to the fluid itself without any additives or metals.

In the system involving the metal washers there are troublesome aspects. Whenever metal washers were present in a mixture under oxidation the best grade of electrolytic metal was used and a standard procedure employed in their preparations for use. Usually attempts were made to express a quantitative effect by noting the change in weight of the test specimen during a run. In the sampling technique no examination could be made until the end of the run and the removal of the metals after the system had cooled.

For a number of years it has been the custom in oxidation studies of this sort to express the weight change of the metals in mg/cm^2. In doing this it should be emphasized that small weight changes as measured to 0.1 mg on an analytical balance are magnified when multiplied by the factor needed to express the change in mg/cm^2. As far as possible in this work, standard procedures for handling the test metals were used, but errors are unadvoidable because of the nature of the procedure.

In this report it does not seem to be worthwhile to report the quantitative data on the metals unless unusual phenomena were observed. For the most part with the amine systems where antioxidant patterns were altered by the presence of copper the attack on the metal was small, and of the order 0.1 to 1.0 mg/cm^2. The general procedure for handling a metal after oxidation is as follows:

First, the metal was washed with benzene and acetone. If this did not remove the film from the oxidized metal, the surface was rubbed somewhat stronger with soft tissue, and then with fine glass wool, with the view of removing only the surface film. However, it was observed that different operators applied varying pressure to the metal surface when trying to remove a film of oxidized fluid or additive. With silver and copper these effects are particularly troublesome and at times some of the metal seemed to be removed with the tissue.

Some recent attention was given to methods of preparing a copper surface before oxidation and more data are needed before definite conclusions can be drawn about the effect of surface preparation on the oxidation. The differences in the effects on the oxidation were slight, but a summary here of the approach is desirable to indicate new directions for research.

In most of the work with copper the surfaces were prepared by cleaning with solvents and with glass wool, followed by rubbing with decreasing fineness grades of metallographic paper and washing in a mixture of iso-octane and acetone. The most promising recent approach to achieving uniform surfaces involved electropolishing and electroplating. Techniques for these were devised almost at the end of the research under this contract and only a few exploratory runs were performed. The polishing bath is an aqueous mixture of copper sulfate containing about 60% phosphoric acid. The use of two cathodes and slow rotation of the copper disks (about one rpm) produced the smoothest polish on the copper surface. After electropolishing to a smooth surface, the disks are copper plated in a solution of copper sulfate and sulfuric acid, using an electrolytic grade copper rod as the anode. This process produces, in preliminary studies, what appears to be a very uniform surface.

To check the freshly plated surfaces and also to compare them with unplated copper disks, both types were used in standard oxidation runs in the absence and presence of dipyridylamine in the diester at 204°C. A Bausch and Lomb Balphot metallograph was used to check the surfaces, with particular emphasis being given to the differences noted between plated and unplated surfaces, both before and after oxidation reaction. The metallograph was also used to examine the copper disks following the various stages of cleaning and weighing, again noting the differences between plated and unplated surfaces.

Preliminary examinations of the plated copper disks with the Balphot metallograph indicate a surface consisting of small grained even copper deposits over the entire area. After the oxidation reaction, irregularities in the surface appear to form more often on the unplated copper disks. For example, at the end of a 24 hour reaction period the plated disks are covered with a smooth oxidation layer, the unplated disks have a large, disorderly deposition

of oxidation products. Investigation of these disks must be continued, to
check that these observations are not just accidental.

(c) Conclusions. Two important aspects of comparing various compounds as
antioxidants and oxidation and corrosion inhibitors on the basis of some function
of their structural formula is being sure of what the formulas are at the
start and what changes each undergo under oxidizing conditions at elevated
temperatures. For the most part, the substances used in this section appear
to have the formulas given in Table II-3, but it must be kept in mind that the
possibilities of isomerism and tautomerism are present with some of the
amines. For example, aminopyridine might be considered as
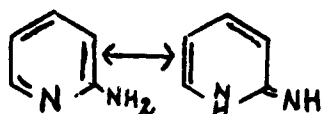
The contributions of each form as the temperature increases is unknown,
but we might speculate that the right hand, or imine, structure is the higher
energy form. The existence of quinoid structures as contributors to the
antioxidant mechanism seems fairly well established in the phenothiazine series.
Similarly with the dipyridylamines, we do not know which are the substances
of primary interest. We might conjecture that this equilibrium is a factor.
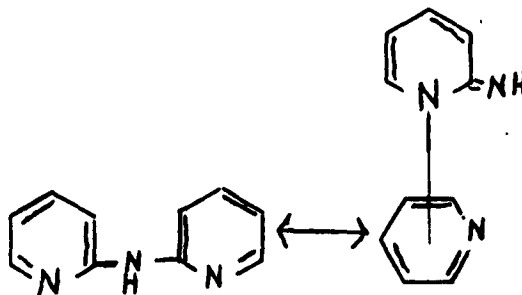
The oxidation of amines in general has been the subject of much research,
but we found the literature sparce on what to expect in the oxidation of substances
like 2, 2'-dipyridylamine. As a fringe phase of the present work, some attention
was given to examination of the mixtures before and after oxidation by infra-red
absorption spectra techniques. It appears that changes do occur as the structures
are exposed to oxidizing conditions at $204^{0}C$, but they are of such a complex nature

that much more work is needed before postulations can be made.

In this section, our endeavors to arrive at some reasonable mechanism for the behavior of the amines is handcapped by the lack of knowledge of both intermediate and final oxidation products. It does appear that many of the amines had very little activity at 204°C, when alone, in preventing viscosity increases on the medium as a result of oxidation. There is, however, a fairly general effect produced by copper when also present in the system under oxidation.

A significant finding is that, during the early period of oxidation in the system 2, 2'-dipyridylamine-copper-di-(2-ethylhexyl) sebacate, the extent of oxidation is about the same both in the presence and absence of metallic copper. However, as the oxidation proceeds it appears that something is being generated in the system which retards the rate of oxidation of the medium. For example, in Table II-2 a mixture containing only 0.17 gram of 2, 2'-dipyridylamine in 100 ml of di-(2-ethylhexyl) sebacate underwent oxidation at 204°C at least as fast as the fluid alone in 24 hours. For longer periods there may be a slower rate so that the fluid with additive after 60 hours may appear to be slightly less oxidized. On the other hand, in the presence of the copper test washers the oxidation retarding activity was evident at 6 hours and rather dramatic after 24 hours. For the practical value of any of the systems, we suggest comparison with the behavior of some of the phenothiazines, which are now widely used and are included here for reference near the end of Table II-2. It should be mentioned also that the sulfur containing additives generally attacked copper more vigorously than the amines and the effect of copper in helping to promote the formation of active antioxidant species is apparent only during the early stages of the oxidation. It might also be noted that other metals such as silver, aluminum, stainless steel and titanium generally did not show the effects observed with copper.

It cannot be stated with certainty that copper itself is not playing a role in retarding oxidations. The electronic structure of copper as a Lewis acid and in mixed oxidation states is interesting. In Table II-2 are shown a summary of experiences with copper in several states and in mixtures of compounds. While both copper I and copper II inorganic compounds have

some activity after 6 hours of oxidation, the lower oxidation state appears slightly more active. This is more evident when the salts are also present with 2, 2'-dipyridylamine and is especially apparent when a copper sulfate, dipyridyl complex was reduced with a alkali hydride and the product examined as an antioxidant. A speculation is that the lower oxidation state, Cu^+, is a better electronic fit with the complex structure retarding the oxidation. This helps explain the delayed action of the metal, because its oxidation mechanism is related to copper I as an intermediate phase and copper oxidizes only slowly at 200^0C. See also Figures II-1 and II-2.

Some complex compounds of copper salts with 2, 2'-dipyridylamine were prepared and studied as a thesis problem by Dennis M. Frame. These were especially effective in retarding the viscosity increases, but they have only low solubility in the diester. A possible practical use for these might be in other fluids and in greases.

The role of coordination complexes of copper is not altogether established because these complexes themselves might also promote, or catalyse, changes in the organic moieties so that the latter serve as the antioxidants. This subject is still an active research here.

The behavior of acids as additives is interesting. A small quantity of H_2SO_4 added to the starting mixture in an aqueous solution appeared to greatly enhance the initial rate of oxidation. This in part could be due to water, but this seems less probable because of the temperature of the reaction. Presumably, most of the water would boil out in a few minutes. Moreover, water is an oxidation product of the system, but it cannot be absolutely eliminated as a factor in either promoting or retarding oxidation if it is strongly bonded to some other species. Copper metal did not appear to assist H_2SO_4 in becoming an oxidation retarding species, nor did it help elementary sulfur in the presence of 2, 2'-dipyridylamine. However, elementary sulfur did change the pattern of 2, 2'-dipyridylamine alone. The data are too limited to even speculate on the possible role of sulfur other than to point out that sulfur has several oxidation states and in low oxidation states is a reducing agent and has metallic properties.

To shed some additional light on the behavior of H_2SO_4 some runs with this in mixture with 2, 2'-dipyridylamine were performed with H_2SO_4 labelled with radioactive sulfur-35. The system was monitored at several stations in the apparatus.

When no copper was present some radioactivity remained in the liquid, but considerable count was noted in the sludge precipitated during the oxidation. Further, as might be expected, the liquid retained on the walls of the overhead refluz condenser showed some radioactivity when the condensers were washed down with acetone at the end of the run. Only small counts above background were obtained in a sodium hydroxide trap at the exhaust end of the condenser. This probably indicates that H_2SO_4 does not break down appreciably to SO_2 and that the sulfate "ion" stays with the oxidation products of dipyridylamine.

In the oxidation cells also containing the copper washers, the counts for the liquid were about the same, but there was a higher count in the washings from the condensers. However, most of the count was associated with the copper washers. There was considerable sludge on the washers and this had a high count, considering internal absorption. Even after washing with acetone and with benzene, the washers retained a high count in a thin, but tough, surface layer. While there was little difference in the appearance of the washers, those which had been prepared by electropolishing and electroplating had a slightly higher count than those prepared by electroplating alone. The significance of this exploratory work with labelled sulfuric acid is not yet clear, but it does appear that considerable additive remains in a complex way associated with the surface. Much more work is needed to tie-down the various speculations on the role of copper and substances which might become Lewis acids in the mixture.

In our work with substituted dipyridylamines, a systematic approach was used to the preparations and evaluations. The patterns of oxidations were generally similar to the parent compound. There were no dramatic phenomena observed, except that copper metal almost invariably appeared to promote, or to enhance the oxidation retarding activity of the amine. There is, however, some indication that the more highly substituted compounds had

at least equal antioxidant activity, but these derivatives may have somewhat less corrosive action on the metal.

The pyridine compounds with a single ring system also showed some enhanced activity in the presence of copper, but in general they seemed to have less attractive features as potential high temperature antioxidants than the dipyridylamines. They are also more volatile.

A samplying of some other organic nitrogen compounds, whose study might be intuitively suggested on the basis of experiences with about 500 additives, is included in Table II-2. Several well-known antioxidants will be recognized, such as diphenylamine and some of its derivatives. In most instances copper had some effect, but its presence did not produce dramatic results.

A few additional comments on some interesting cases might be included here. The presence of two functional groups in adjacent positions in, or on, ring systems produced some anomalies. For example, 2,2'-dipyridyl appeared to have no antioxidant activity even in the presence of copper, but 1, 10 phenanthroline and ortho amino diphenyl did have activity, both in the absence and presence of copper. Quinoline alone was not especially active, but in the presence of copper some activity resulted. Somewhat disconcerting was the finding that 8 hydroxyquinoline was slightly more active than 2-hydroxyquinoline, but both were about like quinoline in the presence of copper.

An effect of adjacent groups is also shown in the aminophenols and in phenylenediamine. In both instances, only the ortho derivatives seemed to be activated significantly by copper. The N-substituted phenylene-diamines have previously been shown to be antioxidants. They are only slightly affected by copper. For the heterocyclic ring systems such as carbazole, acridine and acridone, the data have gaps and on the basis of the available data the effect of copper is most apparent with acridine. With saturated ring systems, such as pyrimidine and dicyclohexylamine, and with five membered rings, such as the oxazoles, there are also indications that copper is promoting oxidation inhibition in the system.

In all of this work with the amines and related substances, the oxidized systems were titrated to a pH of about 8.0 to determine the change in titratable acid. There are no well defined patterns in the absence of copper. Here the acidity increased in 24 hours in most cases up to standard neutralization numbers ranging from 8 to 16 mg KOH per gram of fluid. For those additives for which copper seemed to enhance the antioxidant activity, the neutralization numbers were generally less than without copper, but the values were usually greater than those encountered under analogous conditions with phenothiazine.

The behavior of the peroxides in the systems containing amines and amines and copper were found to be related in part to the elapsed time and temperature between sampling time and the performing of the analysis. In general the standard peroxide numbers were small and so erratic that no significant patterns could be discerned. There is certainly some contribution from peroxides in the oxidation mechanism and the additives change the pattern in some complex way, but other factors are probably more important in the mechanism.

In conclusion, it is reasonable to assume that amines do not have any single mechanism of action as oxidation inhibitors in a diester in the neighborhood of 200°C. As a speculation we will continue to support the mechanistic approach suggested for phenothiazine. That is, some structure, or structures, other than that portrayed by the conventional formula must be generated during the early stages of the oxidation and this is a contribution to the antioxidant action. This might happen as a result of the formation of oxy-species, resonance stabilized free radicals and active species arising from coordination complexes with elements in a low state of oxidation. These active species serve to inhibit peroxide chain oxidations and also serve to interupt the reaction sequence arising from thermal activation. Better answers will not come until more of the gaps are filled in the data with the amines and copper, and a few of these systems are studied in the same detail as was done with phenothiazine. Moreover, in the future more use must be made of tracers as well as the newer techniques for analysis, such as nuclear magnetic resonance and other methods for following free radicals and short-lived species.

FIGURE II-1. Reference Behavior of 2, 2'-Dipyridylamine in Di-(2-ethylhexyl) Sebacate at 204°C

A 0.17 gram per 100 ml, no metals
B 0.17 gram per 100 ml, copper metal
C Reference line of fluid

Time of Oxidation, Hours
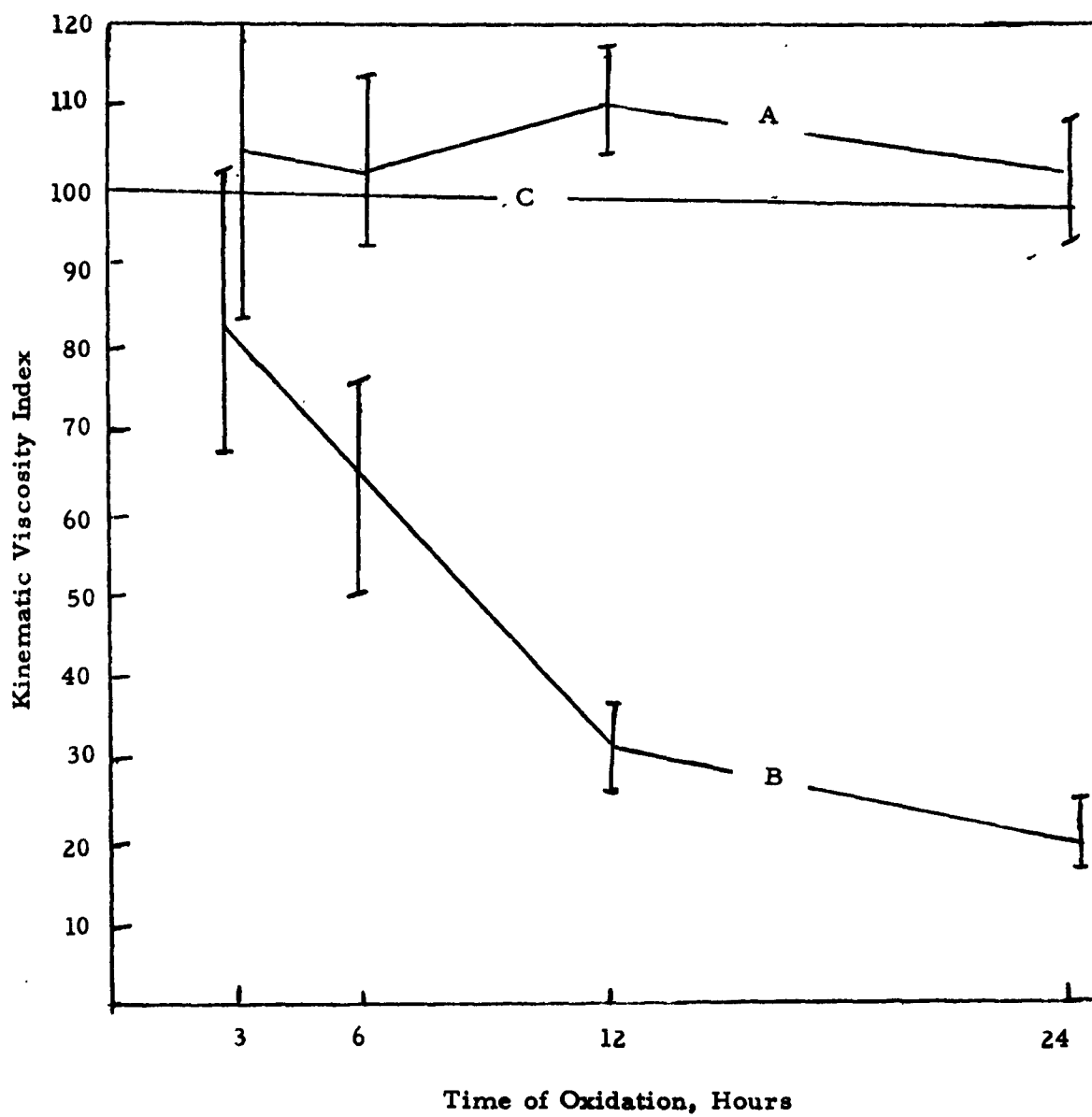
FIGURE II-2 Behavior of 2, 2'-Dipyridylamine in Di-(2-ethylhexyl) Sebacate
with Copper at 204°C

● A   2, 2'-Dipyridylamine alone
○ B   2, 2'-Dipyridylamine and copper metal
◻ C   2, 2'-Dipyridylamine and cuprous chloride
△ D   2, 2'-Dipyridylamine and cupric chloride
⌀ E   Copper sebacate, 2, 2'-Dipyridylamine complex
⌀ F   Copper acetate, 2, 2'-Dipyridylamine complex
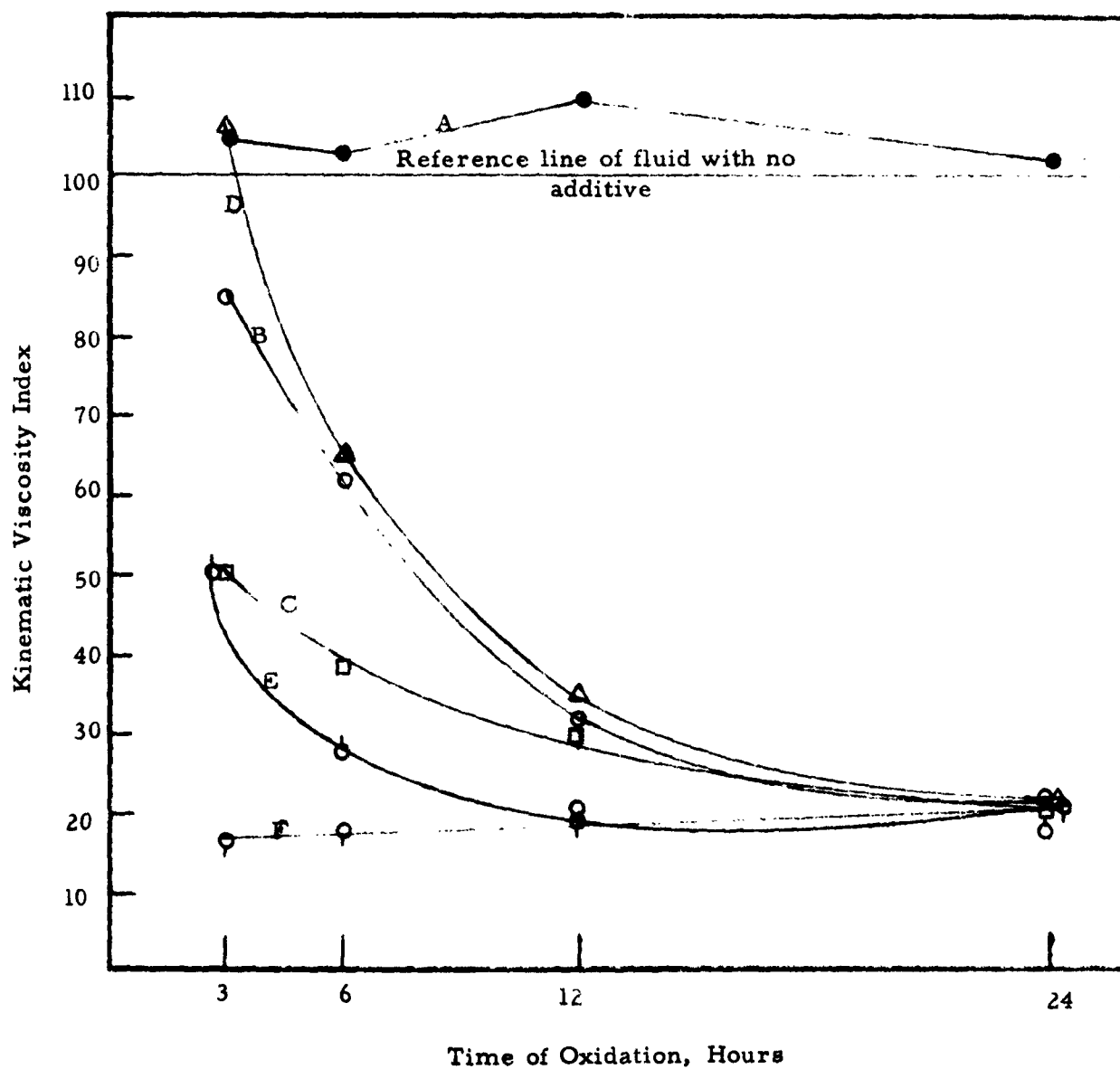
Time of Oxidation, Hours

Table II-2. Oxidation Patterns of Di-(2-ethylhexyl) sebacate at 204°C with Various Additives and Metals.

CCL No., Additive and Concentration	Metals	Viscosity Index at Times (Hours)				
		3	6	12	24	60
128, 2, 2'-Dipyridylamine 0.17	None	105	103	110	102	35
128 0.17	None	137	128	127	128	
128 0.23	None	117	76	100	71	
128 0.45	None	127	119	112	83	
128 0.90	None	110	113	107	72	
128 0.17	3Cu	85	63	31	21	
128 0.23	3 Cu	110	68	33	16	15
128 0.45	3 Cu	107	50	29	18	
128 0.90	3 Cu	104	46	20	19	
128 0.17	1 Cu	131	83	47	22	
128 0.17	1 Cu electroplated	127	79	55	24	
128 0.23	None					30
128 0.90	3 Ag	124	110	92	54	
128 0.22	3 S.S.					25
128 0.22	3 Ti					33
No Additive	3 Cu	108	107	99	97	75
Cuprous Chloride, 0.01	None	110	88	63	44	
Cuprous Chloride, 0.04	None	100	75	59	34	
1 ml 2M H_2SO_4	None	175	95	56	43	
1 ml 2M H_2SO_4	3 Cu	200	150	108	83	
1 ml 2M $CuSO_4$	None	115	118	76	80	
1 ml 2 M $NiSO_4$	None	93	92	100	95	
1 ml 2M $FeSO_4$	None	104	98	112	112	
2, 2'-Dipyridylamine, 0.23 cuprous chloride, 0.01	None	52	38	35	25	
2, 2'-Dipyridylamine, 0.23 cuprous chloride, 0.04	None	35	31	24	22	
2, 2'-Dipyridylamine, 0.45 cuprous chloride, 0.01	None	66	44	33	22	
2, 2'-Dipyridylamine, 0.45 cuprous chloride, 0.04	None	52	23	27	20	
2, 2'-Dipyridylamine, 0.90 cuprous chloride, 0.01	None	48	32	29	20	
2, 2'-Dipyridylamine, 0.45 cuprous chloride, 0.01	3 Cu	38	32	29	20	

Table II-2. Oxidation Patterns of Di-(2-ethylhexyl) sebacate at 204°C with Various Additives and Metals (cont'd)

CCL No., Additive and Concentration	Metals	Viscosity Index at Times (Hours)				
		3	6	12	24	60
Cupric chloride, 0.01	None	130	114	97	73	
Cupric chloride, 0.04	None	110	80	60	41	
2, 2'-Dipyridylamine, 0.23 Cupric chloride, 0.01	None	110	78	42	24	
2, 2'-Dipyridylamine, 0.23 Cupric chloride, 0.04	none	103	51	32	24	
2, 2'-Dipyridylamine, 0.45 Cupric chloride, 0.01	None	105	71	36	17	
2, 2'-Dipyridylamine, 0.45 Cupric chloride, 0.04	None	92	51	31	18	
2, 2'-Dipyridylamine, 0.90 Cupric chloride, 0.01	None	128	75	36	24	
2, 2'-Dipyridylamine, 0.45 Cupric chloride, 0.01	3 Cu	107	59	26	22	
2, 2'-Dipyridylamine, 0.23 Yellow sulfur, 0.08	None	55	56	59	32	
2, 2'-Dipyridylamine, 0.23 Yellow sulfur, 0.08	3 Cu	93	118	111	61	
2, 2'-Dipyridylamine, 0.17 1 ml 2M H_2SO_4	None	100	40	27	21	
2, 2'-Dipyridylamine, 0.17 1 ml 2 M H_2SO_4	1 Cu electropolished	N.M.	146	130	59	
2, 2'-Dipyridylamine, 0.17 1 ml 2 M H_2SO_4	1 Cu electroplated	N.M.	125	123	52	
2, 2'-Dipyridylamine 0.17 1 ml 2 M H_2SO_4	3 Cu	200	170	103	55	
Sebacic acid, 0.04	None	137	118	122	116	
Sebacic acid, 0.04	3 Cu	124	100	84	67	
Sebacic acid, 0.04 Cuprous chloride, 0.01	None	107	78	65	49	
Sebacic acid, 0.04 Cuprous chloride, 0.01	None	127	104	81	55	

Table II-2. Oxidation Patterns of Di-(2-ethylhexyl) sebacate at 204°C with Various
Additives and Metals. (cont'd).

CCL No., Additive and Concentration*	Metals	Viscosity Index at Times (Hours)				
		3	6	12	24	60
152, Copper sebacate, 0.05	None					22
152, 0.06	None	84	74	52	44	
152, 0.10	None	106	81	60	40	46
152, 0.125	None	119.	83	84	33	61
152, 0.40	None	107	87	56	23	60
152, 0.05	3 Cu					100
152, 0.06	3 Cu	97	69	52	66	
152, 0.10	3 Cu	110	81	57	34	65
152, 0.20	3 Cu	103	75	50	19	49
152, 0.40	3 Cu	150	119	56	82	90
Copper sebacate, 0.10 Cuprous chloride, 6.01	None	117	86	58	33	
Copper sebacate, 0.10 Cupric chloride, 0.01	None	110	78	57	35	
395, Copper sebacate 2,2'-Dipyridylamine complex 0.45	None	55	27	27	17	
395, Copper sebacate 2,2'-Dipyridylamine complex 0.45	3 Cu	48	26	28	18	
394, Copper acetate 2,2'-Dipyridylamine complex, 0.37	None	10	20	21	23	10
394 Copper acetate 2,2'-dipyridylamine complex 0.37	3 Cu	17	17	19	19	10
152 Copper sebacate, 0.02 128 2,2'-dipyridylamine, 0.06	None					17
152, 0.02, 128 0.12	None					16
152, 0.02, 128 0.12	None	44	35	36	36	
152, 0.05, 128 0.12	None	20	19	27	34	13
152, 0.05, 128 0.22	None					13
152, 0.12, 128 0.01	None	96	71	56	39	
152, 0.24, 128 0.01	None	63	63	48	39	
152, 0.02, 128, 0.06	3 Cu					20
152, 0.02, 128, 0.12	3 Cu	51	35	39	38	18
152, 0.05, 128 0.12	3 Cu	38	25	34	40	15
152, 0.05, 128, 0.22	3 Cu					12
Unknown product from NaH reaction of copper sulfate, 2,2'-dipyridylamine complex	None	4.2	17	30	39	
152 Copper sebacate, 0.05 52, Diphenylamine, 0.22	None					19
152, 0.05, 128, 0.22	3 Cu					21

Table II-2. Oxidation Petterns of Di-(2-ethylhexyl) sebacate at 204°C with Various
Additives and Metals. (cont'd).

CCL No., Additive and Concentration	Metals	Viscosity Index at Times (Hours)				
		3	6	12	24	60
152, Copper sebacate, 0.05						
293, Phenothiazine, 0.03	None					21
152, 0.05, 293, 0.03	3 Cu					18
2, 2'-Dipyridylamine NiSO₄ complex	None	102	112	112	104	
415, Copper acetate 2-amino-4-methylpyridine complex, 0.34	None	10	13	24	28	
415, 0.34	3 Cu	0	10	20	21	
460, 4,4'-Dipyridylamine, 0.17	None	141	146	127	97	
460, 0.34	None	134	119	115	77	
460, 0.17	3 Cu	114	78	46	17	
460, 0.34	3 Cu	99	63	39	22	
473, 2,4'-Dipyridylamine, 0.17	None	130	129	97	67	
473, 0.34	None	110	126	103	57	
473, 0.17	3 Cu	31	49	38	24	
473, 0.34	3 Cu	55	45	34	29	
452, N-Methyl-2, 2'-Dipyridyl-amine, 0.18	None	145	93	89	78	
452, 0.38	None	84	107	110	105	
452, 0.40	None	85	91	100	86	
452, 0.18	3 Cu	145	107	75	25	
452, 0.38	3 Cu	78	64	29	17	
452, 0.40	3 Cu	117	88	47	19	
478, N-Ethyl-2, 2'-Dipyridyl-amine, 0.20	None	88	78	71	60	
478, 0.20	1 Cu	97	87	81	27	
478, 0.20	3 Cu	137	96	67	38	
480, N-n-butyl-2, 2'-dipyridyl-amine, 0.23	None	98	114	113	108	
480, 0.23	1 Cu	137	96	70	28	
481, N-Acetyl-2, 2'-dipyridyl-amine, 0.21	None	127	118	115	88	
481, 0.21	1 Cu	75	35	45	74	
481, 0.21	3 Cu	155	99	n.m.	91	
472, 5-Methyl-2, 2'-dipyridyl-amine, 0.18	None	74	89	81	69	
472, 0.36	None	62	49	37	41	

Table II-2. Oxidation Patterns of Di-(2-ethylhexyl) sebacate at 204°C with Various Additives and Metals. (cont'd)

CCL No., Additive and Concentration	Metals	Viscosity Index at Times (Hours)				
		3	6	12	24	60
456, 3,3'-Dimethyl-2,2'-dipyridylamine, 0.20	None	159	133	119	117	
456, 0.40	None	133	113	94	68	
456, 0.20	3 Cu	165	83	56	19	
456, 0.40	3 Cu	128	81	35	28	
445, 4,4'-Dimethyl-2,2'-dipyridylamine, 0.05	None	104	112	121	105	
445, 0.10	None	131	133	137	117	
445, 0.20	None	80	117	121	94	
445, 0.40	None	93	100	98	85	
445, 0.05	3 Cu	62	83	49	24	
445, 0.10	3 Cu	93	59	32	20	
445, 0.20	3 Cu	105	56	24	15	
445, 0.40	3 Cu	115	44	20	16	
439, 5,5'-Dimethyl-2,2'-dipyridylamine, 0.05	None	83	113	122	125	
439, 0.10	None	98	122	132	137	
439, 0.20	None	106	113	124	91	
439, 0.40	None	120	118	128	93	
439, 0.05	3 Cu	90	88	74	108	
439, 0.10	3 Cu	107	97	61	35	
439, 0.20	3 Cu	79	54	33	28	
439, 0.40	3 Cu	99	57	29	23	
440, 6,6'-Dimethyl-2,2'-dipyridylamine, 0.05	None	71	98	108	109	
440, 0.10	None	97	97	109	110	
440, 0.20	None	90	113	127	120	
440, 0.40	None	127	105	103	96	
440, 0.05	3 Cu	83	88	83	68	
440, 0.10	3 Cu	74	93	75	117	
440, 0.20	3 Cu	91	77	66	21	
440, 0.40	3 Cu	106	68	54	22	
471, 4,6-Dimethyl-2,2'-dipyridylamine, 0.20	None	74	75	70	107	
471, 0.40	None	88	73	62	56	
471, 0.20	3 Cu	107	67	29	19	
469, 4,4'-6,6'-Tetramethyl-2,2'-Dipyridylamine, 0.23	None	100	107	94	83	
469, 0.23	3 Cu	76	49	21	3.5	

Table II-2. Oxidation Patterns of Di-(2-ethylhexyl) sebacate at 204°C with Various Additives and Metals. (cont'd).

CCL No., Additive and Concentration	Metals	Viscosity Index at Times (Hours)				
		3	6	12	24	60
461						
	None	155	123	120	89	
461, 0.65	None	67	98	77	108	
461, 0.33	3 Cu	148	97	52	34	
461, 0.65	3 Cu	74	88	56	43	
470, N-Methyl-5-methyl 2, 2'-Dipyridylamine, 0.20	None	134	121	114	104	
470, 0.20	3 Cu	123	67	56	32	
447, 2-Methyl pyridine, 0.09	None	66	103	111	104	
447, 0.09	3 Cu	76	96	144	56	
441, 3-Methyl pyridine, 0.09	None	100	114	128	117	
441, 0.22	None	90	114	123	115	
441, 0.09	3 Cu	31	98	95	81	
441, 0.22	3 Cu	86	104	106	93	
466, 2-Bromopyridine, 0.32	None	85	89	66	111	
466, 0.32	3 Cu	46	76	101	59	
459, 3-Bromopyridine, 0.32	None	73	92	97	106	
459, 0.32	3 Cu	75	86	55	68	
449, 2-Hydroxy-3-methyl-pyridine, 0.11	None	83	93	106	92	
449, 0.11	3 Cu	111	93	66	80	
450, 2-Chloro-3-methyl pyridine, 0.13	None	127	70	110	92	
450, 0.13	3 Cu	76	77	72	38	
353, 2-Aminopyridine, 0.10	None	90	110	118	109	50
353, 0.10	3 Cu	80	71	58	20	30
457, 3-Aminopyridine, 0.19	None	130	150	104	94	
457 0.19	3 Cu	174	110	82	42	
458, 4-Aminopyridine, 0.19	None	95	115	108	80	
458, 0.19	3 Cu	117	78	34	35	
255, 2,6-Diaminopyridine, 0.20	None					55
255, 0.20	1 Cu					53
474, N-Methyl-2-amino-pyridine, O.11	None	138	119	119	104	
474, 0.11	3 Cu	128	84	60	30	

Table II-2. Oxidation Patterns of Di-(2-ethylhexyl) sebacate at 204°C with Various Additives and Metals. (cont'd)

CCL No., Additive and Concentration	Metals	Viscosity Index at Times (Hours)				
		3	6	12	24	60
475 N-Ethyl-2-Amino pyridine, 0.12	None	136	123	115	102	
475, 0.12	3 Cu	134	92	56	25	
477, N-isopropyl-2-amino pyridine, 0.14	None	99	106	106	84	
477, 0.14	3 Cu	117	86	51	22	
477, 0.14	1 Cu	125	92	74	40	
479, N-n-Butyl-2-amino pyridine, 0.15	None	95	115	109	104	
479, 0.15	1 Cu	127	65	31	18	
479, 0.15	1 Cu	80	75	61	40	
464, N-Methyl-2-amino-5-methylpyridine, 0.12	None	137	104	110	87	
464, 0.12	3 Cu	123	82	53	34	
105 2-Amino-3-methyl-pyridine, 0.11	None	n.m.	120	119	120	50
105, 0.11	3 Cu	86	78	48	18	30
106, 2-Amino-4-methyl pyridine, 0.11	None	90	115	119	132	44
106, 0.06	3 Cu	93	84	67	31	
106, 0.11	3 Cu	98	79	40	22	34
106, 0.22	3 Cu	66	36	44	50	
107, 2-Amino-5-methyl pyridine, 0.11	None	103	125	125	120	50
107, 0.11	3 Cu	179	84	64	20	20
134, 6-Amino-2-methyl pyridine, 0.11	None					50
134, 0.11	3 Cu					30
454, 5-Amino-2-methoxy-pyridine, 0.12	None	110	111	118	132	
454, 0.12	3 Cu	148	128	122	97	
448, 2-Amino-4,6-dimethyl pyridine, 0.12	None	79	61	116	102	
448, 0.12	3 Cu	140	120	55	15	
451, 2-Amino-5-nitro-6-methylpyridine, 0.15	None	114	117	132	125	
451, 0.15	3Cu	170	n.m.	127	100	

Table II-2. Oxidation Patterns of Di-(2-ethylhexyl) sebacate at 204°C with Various Additives and Metals. (cont'd)

CCL No., Additive and Concentration	Metals	Viscosity Index at Times (Hours)				
		3	6	12	24	60
453-2-Amino-3-nitro-6-methylpyridine, 0.15	None	135	122	120	124	
453, 0.15	3 Cu	125	97	77	91	
407, Quinoline, 0.16	None					120
407, Quinoline, O.16	3 Cu					31
256, 2-Hydroxyquinoline, 0.18	None					140
256, 0.18	3 Cu					28
257, 8-Hydroxyquinoline, 0.18	None					90
257, 0.18	1 Cu					35
257, 0.18	3 Cu					21
52, Diphenylamine, 0.17	None	90	86	94	100	
52, 0.34	None	74	79	79	88	
52, 0.17	3 Cu	86	74	71	53	
52, 0.34	3 Cu	71	52	53	43	
438, p, p'-dimethyl diphenylamine, 0.27	None	93	103	124	115	
438, 0.27	3 Cu	66	78	79	81	
88 Triphenylamine, 0.24	3 Cu	117	110	83	70	102
317, N-Phenylbenzylamine, 0.23	None					77
317, 0.23	3 Cu					32
318, N-Phenyldibenzylamine, 0.34	None					65
318, 0.34	3 Cu					32
412-Dicyclohexylamine, 0.23	None					82
412, 0.46	None					44
412, 0.23	3 Cu					47
412, 0.46	3 Cu					33
412, 0.46	3 Ag					41
412, 0.46	3 Al					38
261, 1-Naphthylamine, 0.18	None					68
261, 0.18	3 Cu					39
262, 2-Naphthylamine, 0.18	None					62
262, 0.18	3 Cu					37

Table II-2. Oxidation Patterns of Di-(2-ethylhexyl) sebacate at 204°C with Various Additives and Metals. (cont'd)

CCL No., Additive and Concentration	Metals	Viscosity Index at Times (Hours)				
		3	6	12	24	60
212, N-Methyl-1-naphthylamine, 0.20	None					58
212, 0.20	3 Cu					49
211-N-Ethyl-1-naphthylamine, 0.22	None					48
211, 0.22	3 Cu					35
38, Di-2-naphthylamine, 0.34	None					44
38, 0.34	3 Cu					33
1B, 2,2'-Dipyridyl, 0.15	None	157	117	111	122	100
1B, 0.15	3 Cu	134	104	98	162	105
405, 2,2',2"-Tripyridyl, 0.23	None	145	124	110	121	
405, 0.23	3 Cu	152	110	67	60	
367, o-Aminodiphenyl, 0.22	None					78
367, 0.22	3 Cu					22
367, 0.22	3 Ag					77
367, 0.22	3 Al					77
406, 1,10-Phenanthroline, 0.24	None					40
406, 0.24	3 Cu					25
Piperidine, 0.43	None	90	100	103	74	
2-Methylpiperazine, 0.50	None	114	114	101	75	
446, N-Acetyl-2,4-dimethyl-aniline, 0.16	None	90	108	112	112	
446, 0.16	3 Cu	114	114	101	75	
434, Benzoic zcid, 0.153	None	100	115	123	110	
434, 0.153	3 Cu	83	104	120	130	
435, Benzamide, 0.17	None	114	127	138	131	
435, 0.17	3 Cu	110	104	82	56	
224, p-Aminobenzoic acid, 0.175	None	166	136	137	130	
224, 0.175	3 Cu	162	133	115	88	70
436, o-Aminobenzoic acid, 0.18	None	169	160	135	125	
436, 0.18	3 Cu	128	120	107	81	

Table II-2. Oxidation Patterns of Di-(2-ethylhexyl) sebacate at 204°C with Various Additives and Metals. (cont'd)

CCL No., Additive and Concentration	Metals	Viscosity Index at Times (Hours)				
		3	6	12	24	60
181A, o-Aminophenol, o.13	None					93
181A, 0.13	3 Cu					36
179A, m-Aminophenol, 0.13	None					84
179A, o.13	3 Cu					150
180A, p-Aminophenol, 0.13	None					80
180A, 0.13	3 Cu					135
433, o-Anisidine, 0.12	None	62	93	121	115	
433, 0.12	3 Cu	86	71	67	34	
444, 2,4-Dimethylaniline acetate, 0.18	None	93	71	100	101	
444, 0.18	3 Cu	48	83	65	31	
442, 2,4-Dimethylaniline, 0.12	None	72	94	127	119	
442, 0.12	3 Cu	69	62	65	29	
183, o-Phenylenediamine, 0.14	None					58
183, 0.14	3 Cu					26
185, m-Phenylenediamine, 0.14	None					82
185, 0.14	3 Cu					52
184, p-Phenylenediamine, 0.14	None					96
184, 0.14	3 Cu					59
40, N,N'-Di-sec-butyl-p-phenylenediamine, 0.28	None					36
40, 0.28	3 Cu					30
186, N,N'-Diphenyl-p-phenylene-diamine, 0.33	None					20
186, 0.33	3 Cu					14
186, 0.33	3 Ag					18
351 N,N'-Dicyclohexyl-p-phenylenediaimne, 0.34	None					44
351 0.34	3 Cu					35
351 0.34	3 Ag					35
352, N-N'-Diphenyl-1,4-benzo-quinonediamine, o.32	None					17
352, 0.32	3 Cu					15
352, 0.32	3 Ag					17

Table II-2. Oxidation Patterns of Di-(2-ethylhexyl) sebacate at 204°C with Various Additives and Metals. (cont'd)

CCL No., Additive and Concentration	Metals	Viscosity Index at Times (Hours)				
		3	6	12	24	60
<u>172</u>, Benzidine, 0.23	None					87
<u>172</u>, 0.23	I Cu					90
<u>340</u> N, N'-Diphenylbenzidine 0.43	None					25
<u>340</u>, 0.43	3 Cu					35
<u>327</u> Diphenylquanidine 0.34	None					46
<u>327</u> 0.34	3 Cu					28
<u>53</u>, Carbazole, 0.21	None					80
<u>53</u>, O.21	3 Cu					150
<u>82</u>, Acridine, 0.12	None					77
<u>82</u>, 0.24	None					48
<u>82</u>, 0.90	None	150	100	76	54	
<u>82</u>, 8.12	3 Cu					14
<u>82</u>, 0.24	3 Cu					13
<u>82</u>, 0.90	3 Cu	100	53	29	21	
<u>57</u> Acridone, 0.25	None					25
<u>57</u> 0.25	3 Cu					33
<u>200</u> 5-Methylisatin, 0.20	None					85
<u>200</u> 0.20	3 Cu					31
<u>177</u> Benzimidazole, 0.15	None					52
<u>177</u> 0.15	3 Cu					25
<u>176</u> 2-Aminobenzimidazole, 0.17	None					35
<u>176</u>, 0.17	3 Cu					42
<u>430</u> 2-Phenyl-4-(<u>alpha</u>-hydroxy-ethylidene)-oxazole-5-one, 0.25	None	138	123	121	104	
<u>430</u> 0.25	3 Cu	135	110	100	76	
<u>433</u>, 2-Phenyl-5-methyloxazole-4-carboxylic acid, 0.13	None	138	120	113	94	
<u>433</u>, 0.26	None	150	134	125	99	
<u>433</u>, 0.13	3 Cu	86	74	51	29	
<u>433</u>, 0.26	3 Cu	76	52	30	20	
<u>437</u> Methyl-2-phenyl-5-methyl-oxazole-4-carboxylane, 0.27	None	107	102	118	118	
<u>437</u>, 0.27	3 Cu	90	81	77	59	

Table II-2. Oxidation Patterns of Di-(2-ethylhexyl) sebacate at 204°C with Various Additives and Metals. (cont'd)

CCL No., Additive and Concentration	Metals	Viscosity Index at Times (Hours)				
		3	6	12	24	60
293, Phenothiazine, 0.20	None	59	31	11	7.4	12
293, 0.25	None	50	30	14	10	10
293, 0.40	None	83	33	15	8.8	10
293, 0.20	3 Cu	41	30	22	49	65
293, 0.25	3 Cu	45	32	16	25	35
293, 0.40	3 Cu	66	44	19	24	30
293, 0.25	3 Ag					12
293, 0.25	3 Al					11
293, 0.25	3 Ti					10
293, 0.25	3 S.S.					12
5, N-Methylphenothiazine, 0.27	None					10
5 0.27	3 Cu					18
5 0.27	3 Ag					11
60 10-Ethylphenothiazine, 0.29	None					9
60 0.29	3 Cu					19
147L 3,7-Dioctylphenothiazine, 0.26	None	107	109	116	104	
147L, 0.26	3 Cu	83	74	60	55	
70 2-Aminobenzenethiol, 0.16	None					19
70, 0.16	3 Cu					75
6a Thianthrene, 0.27	None					123
6a, 0.27	3 Cu					210
54 Phenothioxine, 0.25	None					125
54, 0.25	3 Cu					200
401 4,4'-bisthiopicolinamido-diphenyl, 0.27	None					31
401, 0.27	3 Cu					35
243 Cobalt salt of disalicylal propylenediamine, 0.19	None	45	16	13	11	
476 Copper salt of thiophenyl acetylene, 0.17	None	113	76	55	32	
476, 0.17	1 Cu	97	61	40	29	
476, 0.17	1 Cu unplated	100	76	49	38	
476, 0.17	3 Cu	120	74	77	25	

SECTION III - Sources of Additives

In our work with a variety of additives in synthetic base oils, the materials were either obtained as commerical chemicals, donations as research samples or were synthesized in the Cobb Chemical Laboratory of the University of Virginia. The sources of the substances whose phenomena are summarized in Section I, Table I, were for the most part synthesized here (2, 3, 4). In the work in Section II the point of view was more toward comparing amine additives with structures related to either phenothiazine, pyridine or dipyridylamine. Table III-1 lists the names of the substances used, a probable formula and the source. The symbol "CCL Synthesized" means that the substance was prepared either from existing starting materials by published procedures, or as new compounds in the Cobb Chemical Laboratory. When the substance is apparently a new compound this will be indicated.

A summary of the synthetic methods employed follows. The details of the preparation procedures will be the subject of forthcoming publications.

CCL 5-N-Methylphenothiazine. The procedure was an adaptation of those reported in the literature. Phenothiazine in dry xylene was treated with sodium amide. After refluxing for 5 hours, during which time much ammonia was evolved and a yellow granular solid formed, methyl iodide was added by drops. After three additional hours of refluxing, the hot mixture was filtered, the inorganic salt washed with hot xylene and the solvent removed at reduced pressure. Several recrystallizations from ethanol produced colorless needles, melting point 99-100°C. In the preparation of N-carbon-14-methylphenothiazine for the tracer studies, carbon-14 methyl iodide was used.

CCL 60 - N-Ethylphenothiazine. Essentially the same procedure was followed as in the previous synthesis except ethyl bromide was employed. The product consisted of yellow needles melting over the range 99-100°C.

CCL 147 - 3, 7-Dioctylphenothiazine. This substance was synthesized in order to block the 3, 7 positions which appear to be the active centers for the formation of oxy-species in phenothiazine. The ring was closed by refluxing p, p'-dioctyl diphenylamine and sulfur in the presence of an iodine catalysis.

<u>CCL 293 - Phenothiazine.</u> During the course of our work with antioxidants, phenothiazine from several commerical sources was employed. In order to get a substance of uniform purity, recrystallized diphenylamine was heated with sulfur and iodine to effect the ring closure. After several recrystallizations from an acetone-iso-octane mixture followed by two vacuum sublimations, yellow crystals were obtained melting at 185-185.5^{0}C.

<u>CCL 394 -Copper acetate 2, 2'-dipyridylamine complex.</u> The complex was precipitated from an aqueous mixture of cupric acetate and 2, 2'-dipyridylamine by the addition of enough potassium chloride to produce saturation. Analysis showed 27.3% copper. The presence of a small percentage of water indicates that one mole of water of hydration is probably also present. The color was light greenish blue.

<u>CCL 395 - Copper sebacate-2, 2'-dipyridylamine complex.</u> The complex was salted out of an aqueous mixture of copper sebacate, $CuC_{10}H_{16}O_4$ and 2, 2'-dipyridylamine. The analysis gave 24.4% copper with a molecular weight of about 500. The best correspondence is 1 mole of copper to 1 mole of dipyridylamine.

<u>CCL 415 - Copper acetate-2-amino-4-methylpyridine complex.</u> A mixture oc copper acetate and 2-amino-4-methylpyridine in acetone gave a deep blue solution. Addition of an equal volume of water produced a violet precipitate which contained 1 mole of copper acetate to 1 mole of dipyridylamine and 1 mole of water of crystallization. Drying at 50^0 apparently caused the water to be removed to give a solid with more blue color.

<u>CCL 430 - 2-Phenyl-4-(alpha-hydroxyethylidene)-oxazole-5-one.</u> By modification of the procedure in the literature the yield of this compound was somewhat improved and enough prepared to be used as a starting material for other substances and to be evaluated as an antioxidant.

<u>CCL 433- 2-Phenyl-5-methyloxazole-4-carboxylic acid.</u> CCL 430 was rearranged to the carboxylic acid by treatment of CCL 430 dissolved in a minimum amount of hot 1 normal sodium hydroxide with hydrogen chloride. After evaporation to dryness on a steam bath potassium acetate was added and the mixture mixed in a mortar and pestle. The melt in an open beaker was

stirred until a test portion gave no characteristic color with ferric chloride.
After cooling distilled water was added and the mixture boiled with decolorizing
charcoal. The aqueous filtrate was washed with a small amount of water
and dried. Recrystallization from benzene gave a yield of 70%, melting point
177-180°C, white, fine crystals.

CCL 437 - Methyl-2-phenyl-5-methyloxazole-4-carboxylate. The
later was prepared by reacting diazomethane with CCL 433. Recrystallization
from aqueous alcohol gave fine white needles melting point 80-82°C.

CCL 438 - p,p'-Dimethyldiphenylamine. This was prepared by
elimination of ammonia on refluxing p-toluidine and p-toluidine hydrochloride.
Crystallizations from n-hexene after decolorizing with charcoal gave slender,
colorless needles, melting point 77-78°C.

CCL 439 - 5,5'-Dimethyl-2,2'-dipyridylamine, CCL 440 6,6'-
Dimethyl-2,2'-dipyridylamine, CCL 445 - 4,4'-Dimethyl-2,2'-dipyridylamine
were prepared by refluxing the corresponding methyl derivative of 2-
aminopyridine with its hydrochloride to eliminate ammonia and form the
mixture. The 4,4'-dimethyl-2,2'-dipyridylamine and the 5,5'-dimethyl-
2,2'-dipyridylamine appear to be new. The 6,6'-dimethyl-2,2'-dipyridylamine
was reported in Bielstein 22, II, page 342. Properties: CCL 439 - colorless,
fine needles, melting range 106.5-108°C. CCL 440 - colorless, fine needles
melting range 93.5-95°C, CCL 445 fine colorless crystals, melting range
120-122°C.

CCL 446 - N-Acetyl-2,4-dimethylaniline. was prepared by acetylization
of the parent compound. Recrystallization produced fine white crystals with
a melting range 129.5-131°C.

CCL 449 - 2-Hydroxy-3-methylpyridine and CCL 450 2-Chloro-3-
methylpyridine. For 2-amino-3-methylpyridine was converted to 2-hydroxy-3-
methylpyridine and the latter converted to 2-chloro-3-methylpyridine by the
procedure in Berichte 57, II, 1905 (1924).

CCL 451 - 2-Amino-5-nitro-6-methylpyridine and CCL 454 - 2-
Amino-3-nitro-6-methylpyridine were prepared according to Parker and
Shrive, J. Am.Chem.Soc. 69, 63-7 (1947).

CCL 452 - N-Methyl-2, 2'-dipyridylamine was prepared by refluxing methyl iodine and N-sodium derivative of 2, 2'-dipyridylamine in xylene under dry nitrogen. It is a light yellow liquid boiling at 105-106°C under 2 ml. This substance was also prepared in better yield by the condensation of n-methyl-2-aminopyridine (CCL 474) prepared from sodium hydride with 2-bromopyridine in xylene.

CCL 456 - 3, 3'-Dimethyl-2, 2'-dipyridylamine was prepared by refluxing 2-chloro-3-methylpyridine with N-sodium derivative of 2-amino-3-methylpyridine in xylene under dry nitrogen. Three crystallizations from n-hexane gave a colorless crystalline solid with a melting point range of 126-128°C.

CCL 460- 4, 4'-Dipyridylamine, colorless needles melting range 272-275°C was prepared according to procedure of E. Koenig and G. Jung, J. Fur Praktische Chemie, 137, 145 (1933).

CCL 461 - Quarternary Compound. In the preparation of CCL 452 a second product was isolated which appeared to be a quarternary salt. This substance is still under investigation and other methods of synthesis are being tried in order to get a proof of structure. The formula given has some element of speculation in it.

CCL 464 - N-Methyl-2-amino-5-methylpyridine. colorless liquid, boiling at 221-223°C, was prepared in fair yield by reacting methyl iodide with N-sodium 2-amino-5-methylpyridine in 1, 4-dioxane under dry nitrogen.

CCL 469 - 4, 4', 6, 6'-Tetramethyl-2, 2'-dipyridylamine (white crystals, m.pt. 98.5-99.5°C) was prepared in low yield by reacting equi-molar quantities of 4, 6-dimethyl-2-aminopyridine with its hydrochloride.

CCL 470 - N-methyl-5-methyl-2, 2'-dipyridylamine (light yellow oil, b.pt. 178-180°C at 24 mm) was prepared from the reaction of the sodium salt of N-methyl-2-amino-5-methylpyridine (previously prepared with sodium hydride) and 2-bromopyridine in a minimum of xylene.

CCL 471 - 4, 6-Dimethyl-2, 2'-dipyridylamine (white crystals, m.pt. 82.0-83.0°C) in 40% yield, and CCL 472 - 5-Methyl-2, 2'-dipyridylamine (white crystals, m.pt. 79.5-80.5°C) in 80% yield, were prepared from the reaction of the corresponding sodium salt of the parent compound (parent compound prepared with sodium hydride in xylene) with 2-bromopyridine under nitrogen

atmosphere.

CCL 473 -2,4'-Dipyridylamine (white crystals, m.pt. 182-183°C) was prepared in 40% yield by reacting with sodium salt of 4-aminopyridine (NaH and parent compound in xylene), with 2-bromopyridine. C. Zwart and J.P. Wibaunt, Recueil Des. Trav. Chim. 74, (1955) p. 1081, reported this reaction did not go. They also reported the preparation of 3,3'-dipyridylamine which we have not been able to obtain after several attempts.

CCL 474-N-Methyl-2-aminopyridine (light yellow oil, b.pt. 200-201°C) CCL 475 - N-Ethyl-2-aminopyridine (light yellow oil, b.pt. 206-208°C and CCL 477- N-iso-propyl-2-aminopyridine (white crystals, m.pt. 39.5-40.4°C) were prepared in good yields from the sodium salt of 2-aminopyridine (NaH with parent compound in xylene) followed respectively by reaction with methyl, ethyl and iso-propyl iodide.

CCL 476 - Copper salt of thiophenyl acetylene was prepared by condensing first thiophene and aceto-acetic ester in the presence of phosphoric acid to produce 1-acetylthiophene. The latter yielded a mixture upon treatment with phosphorus pentachloride. The mixture was further treated with sodium amide in liquid ammonia and cuprous chloride added to precipitate the product. This compound is still under investigation in other research projects and is included here because it represents a different type of copper complex. Work with this will be the subject of a separate publication.

CCL 478 - N-Ethyl-2, 2'-Dipyridylamine, light yellow oil, b.p. 130-131°C at 4 mm was prepared in 33% yield by condensing the sodium salt of N-ethyl-2-amino pyridine (CCL 475) prepared from sodium hydride, with 2-bromopyridine in xylene.

CCL 479 - N-n-Butyl-2-aminopyridine, white crystalline plates, m.pt. 43.0-44.0°C was prepared in 52% yield by reacting 1-bromobutane with the sodium salt of 2-aminopyridine, prepared from sodium hydride in xylene,

CCL 480 - N-n-Butyl-2, 2'-dipyridylamine, light yellow oil, b.pt. 178.0-179.5°C at 4 mm. was prepared in 46% yield by reacting the sodium salt of CCL 479, prepared with sodium hydride, with 2-bromopyridine in xylene.

CCL 481 - Acetyl-2, 2'-dipyridylamine. The exact composition of this compound is uncertain because it cannot be stated for sure whether the acetyl group is present on either the ring or the secondary amine nitrogen. When acetic anhydride and acetyl chloride were each refluxed with 3, 3'-dipyridylamine only unchanged starting materials were recovered. However, an interesting reaction was observed with acetyl chloride and the sodium salt of 2, 2'-dipyridylamine. When these were mixed in a flask the color changed from yellow to green and heat was generated. Cooling produced a small amount of solid which is presumably the compound. However, when water was added to the green mixture and unchanged starting material was recovered. Further experiences with this substance will be described later when more experimental evidence is available.

Table III-1. Code Numbers, Formulas and Sources of Additives.
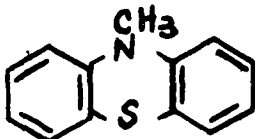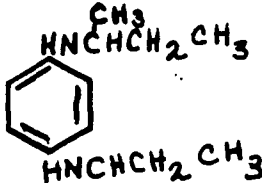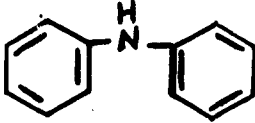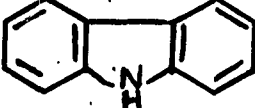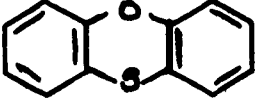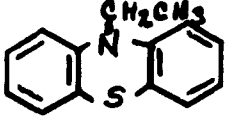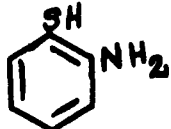
CCL No.	Name	Formula	Source
1B	2, 2'-Dipyridyl		The Matheson Co.
5	N-Methylphenothiazine		CCL Synthesized
6a	Thianthrene		E.I.duPont de Nemours and Co.
40	N, N'-Di-sec-butyl-p-phenylenediamine		Tennessee Eastman Co.
5	Diphenylamine		Eastman Kodak Co.
53	Carbazole		The Matheson Co.
54	Phenothioxine		The Matheson Co.
57	Acridone		The Matheson Co.
60	N-Ethyl phenothiazine		CCL Synthesized
70	2-Aminobenzenethiol		American Cyanamid Co. Eastman Kodak Co.

Table III-1. Code Numbers, Formulas and Sources of Additives. (cont'd)
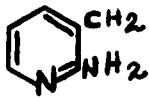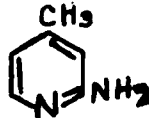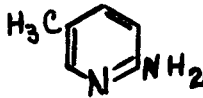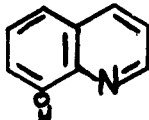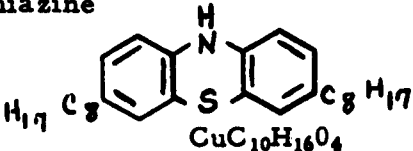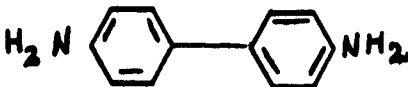
CCL No.	Name	Formula	Source
82	Acridine		The Matheson Co.
88	Triphenylamine	$(C_6H_5)_3N$	Eastman Kodak Co.
105	2-Amino-3-methylpyridine		Reilly Tar and Chemical Corp.
106	2-Amino-4-methylpyridine		Reilly Tar and Chemical Corp.
107	2-Amino-5-methylpyridine		Reilly Tar and Chemical Corp.
109	8-Hydroxyquinoline		Reilly Tar and Chemical Corp.
128	2,2'-Dipyridylamine		Reilly Tar and Chemical Corp.
134	2-Methyl-6-aminopyridine		Reilly Tar and Chemical Corp.
147	3,7-Dioctylphenothiazine		CCL Synthesized
152	Copper sebacate	$CuC_{10}H_{16}O_4$	CCL Synthesized
172	Benzidine		Eastman Organic Chemicals

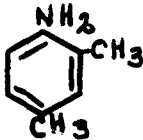Table III-1. Code Numbers, Formulas and Sources of Additives. (cont'd)
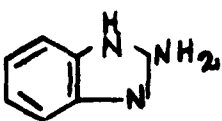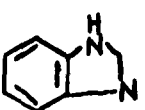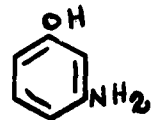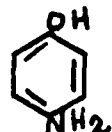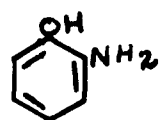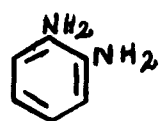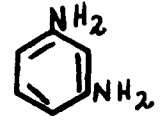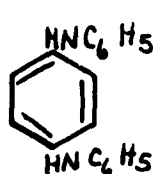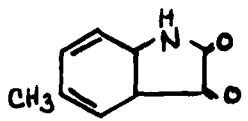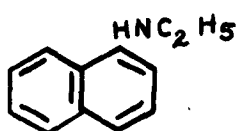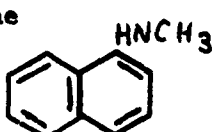
CCL No.	Name	Formula	Source
176	2-Aminobenzimidazole		Eastman Kodak Co.
177	Benzimidazole		Eastman Kodak Co.
179A	m-Aminophenol		Eastman Kodak Co.
180A	p -Aminophenol		Eastman Kodak Co.
181A	o-Aminophenol		Eastman Kodak Co.
183	o-Phenylenediamine		Eastman Kodak Co.
185	m-Phenylenediamine		Eastman Kodak Co.
186	N, N'-Diphenyl-p-phenylene-diamine		Eastman Kodak Co.
200	5-Methylisatin		Eastman Kodak Co.
211	N-Ethyl-1-naphthylamine		Eastman Kodak Co.
212	N-Methyl-1-naphthylamine		Eastman Kodak Co.

Table III-1. Code Numbers, Formulas and Sources of Additives. (cont'd)
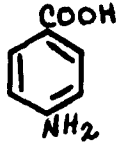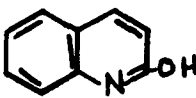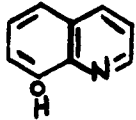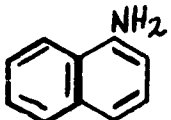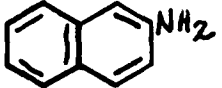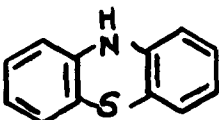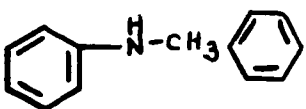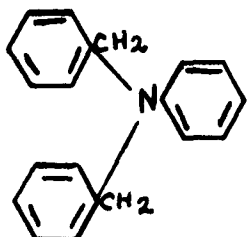
CCL No.	Name	Formula	Source
224	p-Aminobenzoic acid		The Matheson Co.
255	2,6-Diaminopyridine		The Matheson Co.
256	2-Quinolinol		Eastman Kodak Co.
257	8-Quinolinol		Eastman Kodak Co.
261	1-Naphthylamine		Eastman Kodak Co.
262	2-Naphthylamine		Eastman Kodak Co.
293	Phenothiazine		CCL Synthesized
317	N-Phenylbenzylamine		Eastman Organic Chemicals
318	N-Phenyldibenzylamine		Eastman Organic Chemical

Table III-1. Code Numbers, Formulas and Sources of Additives. (cont'd).
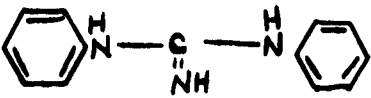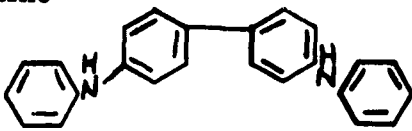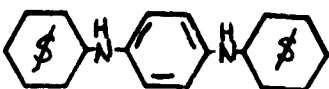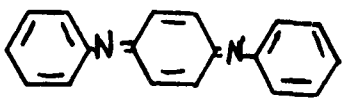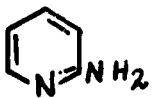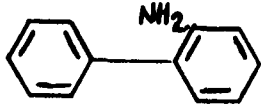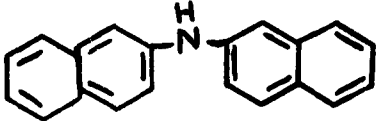
CCL No.	Name	Formula	Source
327	Diphenyl quanidine		Monsanto Chemical Co.
340	N, N'-Diphenylbenzidine		Eastman Organic Chemical
351	N, N'-Dicyclohexyl-p-phenylenediamine		E.I.duPont de Nemours and Co., Jackson Lab.
352	N, N'-Diphenyl-1,4-benzo quinonediamine		E. I. duPont de Nemour and Co., Jackson Lab.
353	2-Aminopyridine		Eastman Kodak Co.
367	o-Aminodiphenyl		Matheson, Coleman and Bell Chemical Co.
383	Di-2-naphthylamine		American Cyanamid Co.
394	Copper acetate-2, 2'-dipyridylamine complex		CCL Synthesized, new
395	Copper sebacate-2, 2'-dipyridylamine complex		CCL Synthesized, new

Table III-1. Code Numbers, Formulas and Sources of Additives. (cont'd)
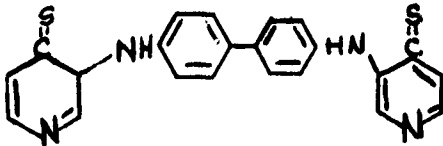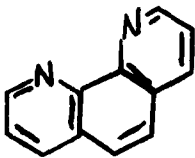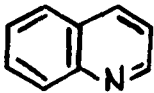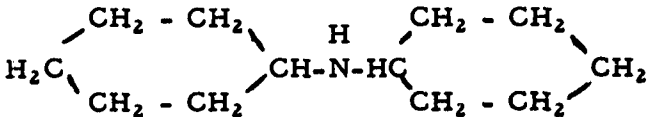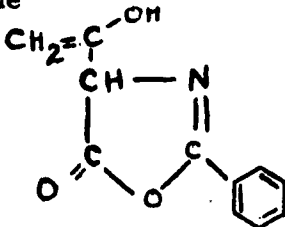
CCL No.	Name	Formula	Source
401	4,4'-Bisthiopicolinamide diphenyl		Wright Air Development Center
405	2,2'2"-Tripyridine		G. Frederick Smith Chemical Co.
406	1,10-Phenanthroline		Eastman Kodak Co.
407	Quinoline		Reilly Tar and Chemical Corp.
412	Dicyclohexylamine		Monsanto Chemical Co.
415	Copper acetate-2-amino-4-methylpyridine complex		CCL Synthesized, new
430	2-Phenyl-4-(alpha-hydroxy-ethylidene)-oxazole-5-one		CCL Synthesized, new

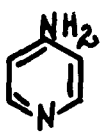Table III.-1. Code Numbers, Formulas and Sources of Additives. (cont'd)
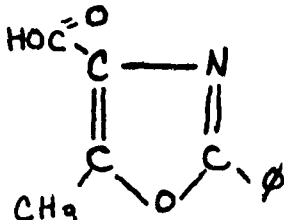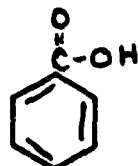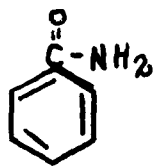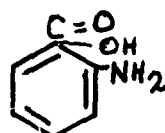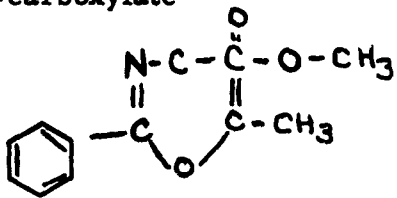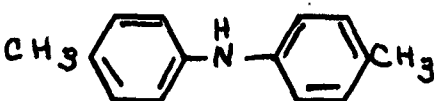
CCL No.	Name	Formula	Source
433	2-Phenyl-5-methyloxazole-4-carboxylic acid		CCL Synthesized
434	Benzoic acid		Allied Chemical and Dye Corp.
435	Benzamide		Eastman Kodak Co.
436	o-Aminobenzoic acid		Eastman Kodak Co.
437	Methyl-2-phenyl-5-methyloxazole-4-carboxylate		CCL Synthesized, new
438	p, p'-Dimethyldiphenyl-amine		CCL Synthesized, new

Table III-1. Code Numbers, Formulas and Sources of Additives. (cont'd)
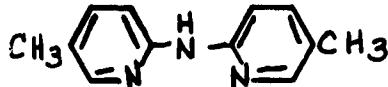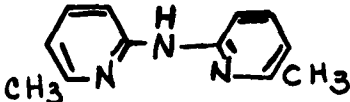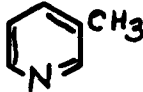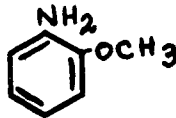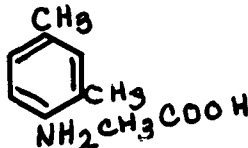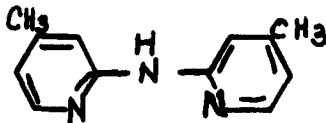
CCL No.	Name	Formula	Source
439	5,5'-Dimethyl-2,2'-dipyridylamine		CCL Synthesized, new
440	6,6'-Dimethyl-2,2'-dipyridylamine		CCL Synthesized, new
441	3-methylpyridine		Eastman Kodak Co.
442	2,4-Dimethylaniline		Eastman Kodak Co.
443	o-Anisidine		Eastman Kodak Co.
444	2,4-Dimethylaniline acetate		Eastman Kodak Co.
445	4,4'-Dimethyl-2,2'-dipyridylamine		CCL Synthesized, new

Table III-1. Code Numbers, Formulas and Sources of Sdditives. (cont'd)
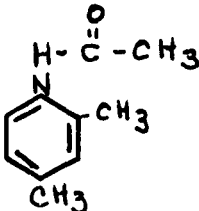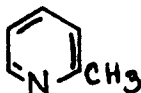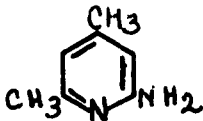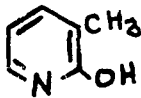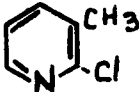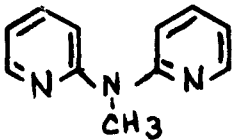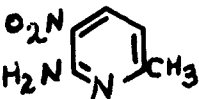
CCL No.	Name	Formula	Source
446	N-Acetyl-2,4-dimethyl-aniline		CCL Synthesized, new
447	1-Methylpyridine		Source Unknown
448	2-Amino-4,6-dimethyl pyridine		Alrich Chemical Co.
449	2-Hydroxy-3-methyl pyridine		CCL Synthesized
450	2-Chloro-3-methylpyridine		Source Unknown
451	2-Amino-5-nitro-6-methylpyridine		CCL Synthesized
452	N-Methyl-2,2'-dipyridylamine		CCL Synthesized
453	2-Amino-3-nitro-6-methylpyridine		CCL Synthesized

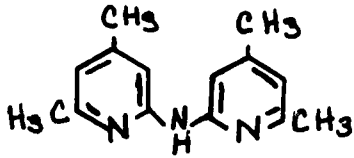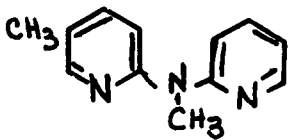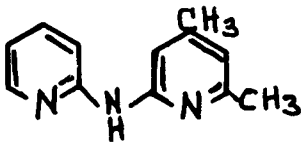Table III-1. Code Numbers, Formulas and Sources of Additives. (cont'd)
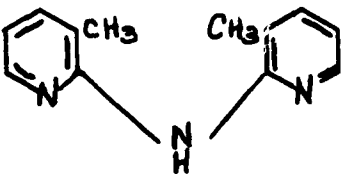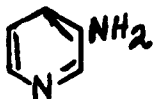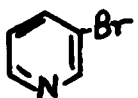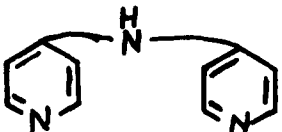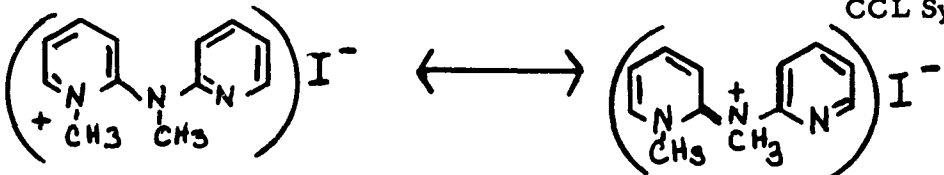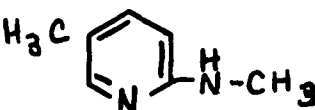
CCL No.	Name	Formula	Source
454	5-Amino-2-Methoxypyridine		Alrich Chemical Co.
456	3,3'-Dimethyl-2,2'-dipyridylamine		CCL Synthesized, new
457	3-Aminopyridine		Reilly Tar and Chemical Corp.
458	4-Aminopyridine		Allied Chemical and Tar Corp.
359	3-Bromopyridine		Reilly Tar and Chemical Corp.
460	4,4'-Dipyridylamine		CCL Synthesized, new
461			CCL Synthesized, new
464	N-Methyl-2-amino-5-methylpyridine		CCL Synthesized, new

Table III-1. Code Numbers, Formulas and Sources of Additives. (cont'd).
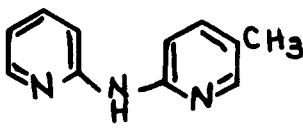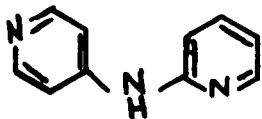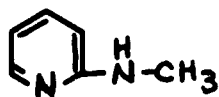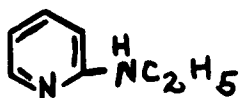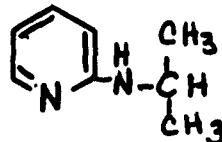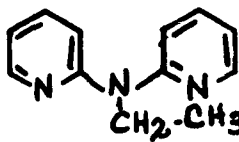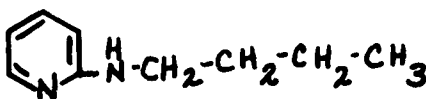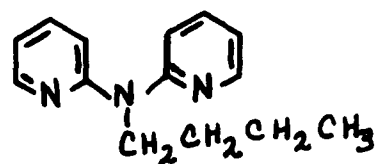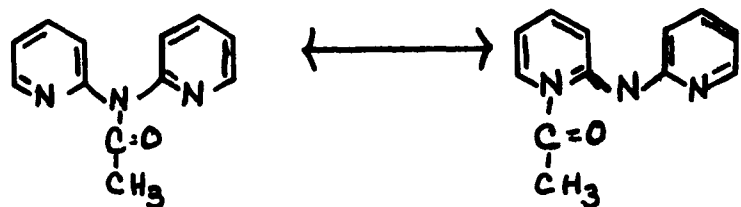
CCL No.	Name	Formula	Source
466	2-Bromopyridine		Reilly Tar and Chemical Corp.
469	4,4',6,6'-Tetramethyl-2,2'-dipyridylamine		CCL Synthesized, new
470	N-Methyl-5-methyl-2,2'-dipyridylamine		CCL Synthesized, new
471	4,6-Dimethyl-2,2'-dipyridylamine		CCL Synthesized, new
472	5-Methyl-2,2'-Dipyridylamine		CCL Synthesized, new
473	2,4-Dipyridylamine		CCL Synthesized, new
474	N-Methyl-2-aminopyridine		CCL Synthesized, new
475	N-Ethyl-2-aminopyridine		CCL Synthesized, new

Table III-1. Code Numbers, Formulas and Sources of Additives. (cont'd)

CCL No.	Name	Formula	Source
476	Copper salt of thiophenyl acetylene		CCL Synthesized, new
477	N-isopropyl-2-amino-pyridine		CCL Synthesized, new
478	N-Ethyl-2, 2'-dipyridylamine		CCL Synthesized, new
479	N-n-butyl-2-aminopyridine		CCL Synthesized, new
480	N-n-butyl-2, 2'-dipyridyl-amine		CCL Synthesized, new
481	Acetyl-2, 2'-dipyridylamine		CCL Synthesized, new

SECTION IV Bibliography

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